Marangoni Contraction of Evaporating Sessile Droplets of Binary Mixtures

Supplemental Material

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APPARENT CONTACT ANGLES

In the main manuscript, only a few apparent contact angle data were shown to demonstrate the trends with respect to relative humidity and mixing ratio. Here we show all experiments that were used in the further analysis of the contraction behavior. Fig. S1 shows the measured apparent contact angle as a function of relative humidity (symbols). The lines depict the fit of Eq. (1) of the main manuscript to each dataset. Each panel shows a different type of diol, Ethylene Glycol (1,2-Ethanediol, panel A), Propylene Glycol (1,2-Propanediol, panel B), and 1,2-Butanediol (panel C).

EQUILIBRIUM RELATIVE HUMIDITY

Figure S2 shows the equilibrium relative humidities that were determined from fitting Eq. (1) of the main manuscript to the measured contact angles shown in Fig. S1. The lines correspond to the behavior of (thermodynamically) ideal mixtures, where, for entropic reasons, the equilibrium vapor pressure scales linearly with the mass fraction of the volatile component in the liquid.
SIMULATIONS

In lubrication approximation [2, 3], the evolution equations for height $h(r)$ and vertically averaged mass fraction $\phi(r)$ of a radially symmetric thin liquid film are given by equations (2-5) of the main manuscript. The kernel $\kappa(r, r')$ in Eq. (6) of the main manuscript is [3]

$$\kappa(r, r') = 4 \begin{cases} r & [K(r/r') - E(r/r')] \quad r' < r \\ r' & [K(r/r') - E(r/r')] \quad r' > r \end{cases} .$$  \hspace{1cm} (1)

The pressure-dependent term in Eq. (6) of the main manuscript, together with the disjoining pressure from Eq. (5) of the main manuscript, ensures quasi-equilibrium between the precursor film and the vapor above it. In the experimental settings, typical ratios of precursor thickness $h_f$ to droplet heights $h_0$ are on the order of $h_f/h_0 \sim 10^{-6}$. Hence, I) hydrodynamic processes in the precursor are practically irrelevant on the time scale of the droplet profile evolution, and II) on the latter time scale, the precursor film adapts by evaporation or condensation almost instantaneously to changes in the vapor field because the corresponding height changes / mass exchanges are small. Thus, Eqs. (5,6) of the main manuscript establish an effective “no-flux” boundary condition for the vapor at the substrate around the droplet. In order to obtain manageable simulations times, while keeping the separation of scales as large as possible, we chose $h_f/h_0 \sim 10^{-5}$ for most of the simulations. Four control runs with experimental $h_f/h_0 \sim 10^{-6}$ were preformed and showed nearly identical results.

The evolution equations are complemented with a no-flux boundary condition at $r = 0$, and, at large $r$ (typically 20 times the droplet radius), an equilibrium condition for the ambient humidity. The evaporation integral is continued beyond the simulation domain with the analytical solution for a homogeneous droplet with identical radius and identical average composition [3]. Simulation profiles are continuous between drop and precursor (cf. Fig. S3). To estimate an apparent contact angle, we use $\Theta_{app} = 2h_{drop}/R_{drop}$, where the drop radius is defined by the peak in capillary pressure.

We non-dimensionalize $h$ with $h_f$, the precursor film thickness far from the droplet [3], and chose the radial length scale $r_0 = h_f^2/a$ to obtain a parameter-free pressure term. The time scale $t_0 = 3\eta h_f^3/(\gamma_0 h_f^3)$ eliminates the prefactor of the pressure-driven flux term. The di-
Dimensionless equations are
\[ \partial_t h = \frac{1}{r} \partial_r \left\{ r \left[ h^3 \partial_r p + \mathcal{M} h^2 \partial_r \phi \right] \right\} - \mathcal{E} j, \]  
\[ \partial_t (\phi h) = \frac{1}{r} \partial_r \left\{ r \phi \left[ h^3 \partial_r p + \mathcal{M} h^2 \partial_r \phi \right] + 3 r \partial_r \partial_r \phi \right\}, \]
with
\[ p = - \left\{ \frac{1}{r} \partial_r \left[ r \partial_r h \right] + \frac{1}{h^3} \right\}, \]  
\[ j = - \frac{1}{r} \partial_r \int_0^\infty \kappa(r, r') \partial_r p_v \, dr', \]  
\[ p_v = (1 - x)(1 + \alpha p), \]
and the non-dimensional parameters
\[ \mathcal{M} = \frac{3 \Delta \gamma r_0^2}{2 \gamma_0 h_f^2}, \quad \text{(Marangoni Number)} \]  
\[ \mathcal{D} = \frac{3 D \eta r_0^2}{\gamma_0 h_f^2}, \quad \text{(Peclet Number)} \]  
\[ \mathcal{E} = \frac{3 \eta D_v p_{sat} r_0^3}{\gamma_0 \rho h_f^4}, \quad \text{(Evaporation Number)} \]  
\[ \alpha = \frac{M_w}{M_D}, \quad \text{(Molar Mass Ratio)} \]

Spatial discretization is performed according to known stable, convergent schemes that conserve mass and non-negativity of the height profile. We use numerical mobilities that correspond to a harmonic average of the mobility between neighboring grid points, which has been shown to converge to the evolution of the continuous equation \[4, 5\]. We used a strongly graded grid where the grid spacing varied by a factor of 8000 between the contact line (finest) and the regions far from the droplet (coarsest). Time integration is performed with the splitting scheme proposed in \[5\], with an additional explicit step for evaporation.

The simulations are initialized with homogeneous droplets of different mass fractions from \( \phi_0 = 10^{-3} \) to 0.9, ambient relative humidities from \( \text{RH} = 0 \) to 0.9, and an apparent contact angle of 20°.

Fig. S3 shows, in addition to fig. (4) of the main text, drops in quasi-stationary conditions for several average diol massfractions.

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