Supplementary Information: Spreading dynamics of reactive surfactants driven by Marangoni convection

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In these notes, we give some technical details regarding the derivation of equations (5) and (9).

I. CLOSURE RELATION FOR THE INTERFACIAL VELOCITY

Since the Stokes equations are linear, one expects a linear relationship between the interfacial velocity and the concentration [1, 2]. In the Stokes regime, the velocity field $\mathbf{v}(x,z) = v_x(x,z)\mathbf{e}_x + v_z(x,z)\mathbf{e}_z$ obeys the equations

$$\eta \nabla^2 \mathbf{v} = \boldsymbol{\nabla} p \ , \quad \text{and} \quad \boldsymbol{\nabla}\cdot\mathbf{v} = 0 \ , \tag{1}$$

together with the boundary conditions (BCs)

$$v_z\big|_{z=0} = 0 \ , \tag{2a}$$

$$\eta\left(\partial_z v_x + \partial_x v_z\right)\Big|_{z=0} = -\gamma_1 \frac{\partial_x \Gamma}{\Gamma_0} \ . \tag{2b}$$

Define the Fourier transform of $f(x)$ as

$$\tilde{f}(q) = \mathcal{F}[f(x)] = \int_{-\infty}^{\infty} f(x) e^{-iqx} \mathrm{d}x \ ,$$

the Stokes equations can be rewritten as

$$\eta\left(-q^2 \tilde{v}_x + \partial_z^2 \tilde{v}_x\right) = iq\tilde{p} \ , \tag{3a}$$

$$\eta\left(-q^2 \tilde{v}_z + \partial_z^2 \tilde{v}_z\right) = \partial_z \tilde{p} \ , \tag{3b}$$

$$iq\tilde{v}_x + \partial_z \tilde{v}_z = 0 \ , \tag{3c}$$

and the BCs at the free interface now read

$$\tilde{v}_z(q,0) = 0 \ , \tag{4a}$$

$$\partial_z \tilde{v}_x\big|_{z=0} = -iq\frac{\gamma_1}{\eta\Gamma_0}\widetilde{\Gamma}(q) \ . \tag{4b}$$

After some algebra, one can show that eqn (3) can be recast in a single equation for the vertical component of the velocity

$$\left(\partial_z^4 - 2q^2\partial_z + q^4\right)\tilde{v}_z = 0 \ .$$

The liquid being confined to the half-space $z < 0$, the solution that satisfies the BC (4a) is

$$\tilde{v}_z(q,z) = Bze^{|q|z} \ .$$

According to eqn (3c), the horizontal component is obtained as

$$\tilde{v}_x(q,z) = \frac{iB}{q}\left(1 + |q|z\right)e^{|q|z} \ .$$

Enforcing the Marangoni BC (4b), one finally gets

$$B = -\frac{\gamma_1}{2\eta\Gamma_0}\frac{q^2}{|q|}\tilde{\Gamma}(q) \ .$$

In particular, the interfacial velocity is obtained in Fourier representation

$$\tilde{v}_x(q,0) = -i\frac{\gamma_1}{2\eta\Gamma_0}\mathrm{sgn}(q)\tilde{\Gamma}(q) \ . \tag{5}$$

The inverse transform then involves a convolution product

$$v_x(x,0) = \frac{\gamma_1}{2\eta\Gamma_0}\int_{-\infty}^{\infty}\mathrm{d}x'\Gamma(x')K(x-x') \ ,$$

with $K(x) = \mathcal{F}^{-1}[-i\mathrm{sgn}(q)] = 1/(\pi x)$, so that one eventually gets the desired relation

$$v_x(x,0) = \frac{\gamma_1}{2\eta\Gamma_0}\int_{-\infty}^{\infty}\mathrm{d}x'\frac{\Gamma(x')}{\pi(x-x')} \ . \tag{6}$$

Note that the improper integral is understood in the sense of the principal value.

II. PROPERTIES OF HILBERT TRANSFORMS

The Hilbert transform of a function $f(x)$ is defined as [3]

$$\mathcal{H}[f(x)] = \frac{1}{\pi}⨍_{-\infty}^{\infty}\frac{f(y)}{x-y}\mathrm{d}y \ , \tag{7}$$

where the dashed integral refers to the Cauchy principal value. The Hilbert transform satisfies the following properties [3]

$$\mathcal{H}\left[\partial_x f\right] = \partial_x \mathcal{H}[f(x)] \ , \tag{8a}$$

$$\mathcal{H}\left[xf(x)\right] = x\mathcal{H}[f(x)] - \int_{-\infty}^{\infty} f(u)\mathrm{d}u \ . \tag{8b}$$

In the following, we shall consider the function $g(x)$ defined as

$$g(x) = \begin{cases} \sqrt{\xi^2 - x^2} & \text{for} \quad |x| < \xi \ , \\ 0 \quad \text{otherwise} \ . \end{cases}$$

Taking the Hilbert transform, we therefore get

$$\mathcal{H}[g(x)] = \begin{cases} x \quad \text{for} \quad |x| < \xi \ , \\ x - \mathrm{sgn}(x)\sqrt{x^2 - \xi^2} & \text{otherwise.} \end{cases}$$

Moreover, according to Eq. (8b), we also have

$$\mathcal{H}[xg(x)] = \begin{cases} x^2 - \frac{\xi^2}{2} & \text{for} \quad |x| < \xi \ , \\ x^2 - \frac{\xi^2}{2} - |x|\sqrt{x^2 - \xi^2} & \text{otherwise.} \end{cases}$$

III. DERIVATION OF THE TIME EVOLUTION EQUATIONS FOR $\mathcal{A}(t)$ AND $\xi(t)$.

In rescales variables, the concentration of surfactants obeys the following nonlinear equation

$$\partial_t \Gamma + \partial_x \left(\Gamma \mathcal{H}[\Gamma] \right) = -\alpha \Gamma \ . \tag{9}$$

Inspired by previous work [1, 2], we consider a semi-circle distribution

$$\Gamma(x,t) = \mathcal{A}(t) \sqrt{\xi^2(t) - x^2} \ , \tag{10}$$

for $|x| < \xi(t)$, and $\Gamma(x,t) = 0$ otherwise. Here, $\mathcal{A}(t)$ and $\xi(t)$ are two positive functions. We get for this particular choice the relation

$$\Gamma(x,t) \mathcal{H}[\Gamma(x,t)] = \mathcal{A}(t) x \Gamma(x,t) \ .$$

The derivation then consists in taking the Hilbert transform of eqn (9) with $\Gamma(x,t)$ defined by (10). We first proceed in the domain $|x| < \xi(t)$. Making use of eqn (8a), its is straightforward to obtain

$$x \left(\dot{\mathcal{A}} + 2\mathcal{A}^2 + \alpha \mathcal{A} \right) = 0 \ .$$

But this equation has to be satisfied for all $|x| < \xi(t)$: the term between parenthesis must necessarily vanish, leading to the first equation

$$\dot{\mathcal{A}} + 2\mathcal{A}^2 + \alpha \mathcal{A} = 0 \ . \tag{11}$$

We proceed in the same manner for $|x| > \xi(t)$: although the algebra is slightly more tedious, the Hilbert transform of eqn (9) now leads to

$$\left(x^2 - \xi^2 \right) \left(\dot{\mathcal{A}} + 2\mathcal{A}^2 + \alpha \mathcal{A} \right) = \mathcal{A} \xi \left(\dot{\xi} - \mathcal{A} \xi \right) \ ,$$

so that we get the second equation

$$\dot{\xi} = \mathcal{A} \xi \ . \tag{12}$$

We therefore end up with a set of ordinary differential eqns (11)–(12) that, even though nonlinear, is tractable analytically using standard technics.

[1] A. Thess, D. Spirn and B. Jüttner, *Phys. Rev. Lett.*, 1995, *75*, 4614–4617.
[2] A. Thess, D. Spirn and B. Jüttner, *J. Fluid Mech.*, 1997, *331*, 283–312.
[3] R. Piessens, The Hankel Transform. In *Transforms and Applications Handbook*, CRC Press, 2010.