ON TWO MINIMALIST MODELS FOR MOVING/EVAPORATING CONTACT LINES WITHOUT SLIP ON A MACROSCOPICALLY DRY HOMOGENEOUS SUBSTRATE

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Summary We consider two minimalist models allowing self-consistent analyses of contact-line (micro)structures starting abruptly on a macroscopically bare solid surface in the hydrodynamic framework without any slip lengths or extended precursor films. The motion- and/or evaporation-induced apparent contact angles are discussed. One model, inspired by de Gennes and collaborators, invokes the disjoining pressure, while the other manages without this concept but requires the Kelvin effect and a pure-vapour atmosphere.

The mathematical and numerical modelling of macroscopic transport phenomena involving three-phase contact lines still faces important difficulties nowadays, due to singularities of various origins. On the one hand, at a moving contact line, there is a well-known divergence of the viscous stress, which results from the explicit assumption that the distance between the moving interface and the (say) motionless solid boundary vanishes at some location. On the other hand, for the volatile liquids also considered in this study, a similar singularity of the heat flux (and of the phase change rate) may occur as well in the framework of the simplest classical models. It is also well-known that both these non-integrable singularities can be regularized (or at least rendered integrable), by a number of small-scale effects (e.g. Navier slip for the first one, kinetic resistance to phase change for the second, extended precursor films for both of them), not to mention mesoscopic and/or molecular-scale approaches clearly beyond our scope here. In the present contribution, we will not assume any of these effects to enter the continuum lubrication-type description, and stick to situations such that there is a point of the substrate where the film thickness vanishes, hence separating a wet region from the macroscopically "bare" ("dry") surface. The possibility of molecular-scale adsorption on the latter, if any, will be accounted for by using the appropriate solid-gas surface energy (i.e. we consider it as Gibbs adsorption).

Two different models will be reviewed and, to some extent, compared with each other. The first one relies on the use of a disjoining pressure of the usual apolar form, namely $\Pi^* = A^*/\xi^{*3}$ with $A^* > 0$ (ξ^* denoting the film thickness), in combination with a given spreading coefficient $S^* = \gamma_{sg}^* - (\gamma_{sl}^* + \gamma^*)$, where γ_{sg}^*, γ_{sl}^* and γ^* are the solid-gas, solid-liquid and liquid-gas interfacial tensions, respectively. Such a "paradigm" has been originally used by de Gennes [1] and collaborators in the framework the lubrication (thin-film) approximation. They applied it not only to study equilibrium film profiles [1], but also advancing contact lines of non-volatile liquids [1,2] in the perfectly wetting case ($A^* > 0$ and $S^* > 0$). The latter work in particular shows that the viscous stress singularity can be rendered integrable, as far as physically meaningful quantities (such as the total force exerted on the substrate and the viscous dissipation) are considered, even though the film profile near the tip, $\xi^* \sim (x^* - x_0^*)^{1/2}$, is itself singular. As discussed in [3], curiously enough, it is the singular form of the disjoining pressure ($\Pi^* = A^*/\xi^{*3}$ applied down to vanishing thicknesses) that renders otherwise non-integrable singularities integrable. The remaining singularities, although integrable, indicate that the consideration must break down in a certain tiny (molecular-scale) vicinity of the tip. Further regularization effects can in principle be considered therein, even though they are not deemed to be essential globally for the contact-line microstructure. The model turns out to be quite versatile, applying to a variety of situations with complete ($S^* > 0$) or partial ($S^* < 0$) wetting, with or without phase change (into a pure vapour phase or an inert gas), with or without some additional effects (e.g. the kinetic resistance to phase change, the Kelvin effect) [3]. In the present short note, however, we shall look at it first of all from a "minimalist" point of view, dropping out the effects that are not essential for the resolution of the classical non-integrable singularities. Besides, in the volatile case, we shall here limit ourselves to a pure-vapour atmosphere, as it is the case as well for the second model we deal with here.

This second model does not make use of a disjoining pressure, albeit it is limited to the volatile case with pure vapour and requires the Kelvin effect (the dependence of the saturation pressure on the curvature) for the resolution of the classical contact-line singularities. It is conceptually important and remarkable per se that such a resolution can be accomplished entirely in the framework of classical physics, and we shall here stick first of all to a minimalist description for this second model too. We note that, unlike the first one, the second model does not involve singularities at all, not even integrable.

In the case of a pure-vapour atmosphere we limit ourselves to here, the evaporation is globally determined by the superheat value ΔT^*, which is the difference between the substrate temperature and the saturation temperature T_0^* corresponding to a given pressure of the vapour. The particular case $\Delta T^* = 0$, with no superheat, is formally equivalent to the non-volatile case in the framework of the first minimalist model. There is no such complete equivalence for the second model, however, where even for $\Delta T^* = 0$ some phase change can be induced by the Kelvin effect, albeit of a local nature, in a small vicinity of the contact line. Nonetheless, it is in fact this local phase change that provides the corrective effect resolving the classical singularities.

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We shall be interested in stationary 2-d film profiles (contact-line microstructures) starting at some $x^* = x_0^*$ (such that the bare/dry parts of the solid surface correspond to $x^* < x_0^*$) and translating at a constant velocity $c^* = -dx_0^*/dt^*$ ($c^* > 0$ – advancing, $c^* < 0$ – receding). Thus, $\xi^* = \xi^*(\tilde{x}^*)$ with $\tilde{x}^* = x^* + c^* t^*$. We shall take $\tilde{x}^* = 0$ at the starting point and hereafter omit the tilde. The asterisk marks the dimensional quantities. The dimensionless ones appear without asterisk. For the typical quantity f we thus have $f^* = [f]f$, where $[f]$ is the scale. The dimensionless lubrication equation for $\xi = \xi(x)$ that encompasses both models in their minimalist form can be written as (e.g. [3])

$$c\,\xi' + \tfrac{1}{3}\Big(\xi^3\big(3\xi'' + A\,\Pi(\xi)\big)'\Big)' + \frac{E - \mathcal{K}\,\big(3\xi'' + A\,\Pi(\xi)\big)}{\xi} = 0$$

where

$$\varepsilon = \frac{[\xi]}{[x]} \ll 1, \qquad c = \frac{3\,Ca}{\varepsilon^3}, \qquad Ca = \frac{\mu_l^* c^*}{\gamma^*} \ll 1\,, \qquad A = \frac{3A^*}{\varepsilon\,\gamma^*[\xi]^2}\,, \qquad E = \frac{3\,Ca_{\mathrm{evap}}}{\varepsilon^4}\,,$$

$$Ca_{\mathrm{evap}} = \frac{\mu_l^* \lambda_l^* \Delta T^*}{\gamma^* \rho_l^* \mathcal{L}^* [\xi]} \ll 1\,, \qquad \mathcal{K} = \frac{\mu_l^* \lambda_l^* T_0^*}{\rho_l^{*2} \mathcal{L}^{*2} [\xi]^2 \varepsilon^2}\,,$$

and the prime denotes a derivative with respect to x. Here ρ_l^*, μ_l^*, λ_l^* and $\mathcal{L}^*$ are density, dynamic viscosity, thermal conductivity and latent heat of evaporation, respectively. E is the evaporation number, A and $\mathcal{K}$ are the dimensionless numbers corresponding to the disjoining-pressure and Kelvin-effect contributions. It is explicitly indicated that certain numbers must be small in accordance with the approximation used, whereas the others can in principle be $O(1)$. The scales $[\xi]$ and $[x]$ are not yet concretized. One of the boundary conditions for both considered models is $\xi = 0$ at $x = 0$ (and besides we assume no mass source at this point). We remind that neither the slip, nor the effect of kinetic resistance to phase change (which would modify the denominator of the phase-change term from ξ to $\xi + K$, where $K = O(1)$ is the appropriate kinetic-resistance number, e.g. [3]) are included in the present minimalist version. In particular, this leaves a clearly singular denominator, hence an "extreme" situation in some sense.

Now the minimalist version of the first model corresponds to $\mathcal{K} = 0$, whereas $A \neq 0$ and we use $\Pi(\xi) = 1/\xi^3$. In fact, the scales $[\xi]$ and $[x]$ can be concretized such that $A \equiv 1$, and either $|c| \equiv 1$ or $|E| \equiv 1$, depending on whether the accent is over the motion-induced or phase-change-induced effects. Note that the non-volatile case corresponds here to $E = 0$ ($\Delta T^* = 0$), and we can choose $|c| \equiv 1$. For immobile contact lines, $c = 0$, and we can choose $|E| \equiv 1$ in order to study motionless contact-line structures with phase change, and in particular the evaporation-induced apparent contact angles. Using the equation, one can show that the film profile starts as $\xi = (2^{1/2}/3^{1/4})\,x^{1/2}[1 - (3^{1/2}/4)\,\Sigma\,x - (2^{1/2}3^{3/4}/5)(c + 3^{1/2}E)\,x^{3/2}\log x - (2^{3/2}/5 \times 3^{3/4})\,\Omega\,x^{3/2} + \cdots$ as $x \to 0$, involving integrable singularities. One of the coefficients, Ω, is here free and must be determined by boundary conditions at larger x (e.g. a condition of zero curvature as $x \to +\infty$). The other coefficient, Σ, gets identified with the dimensionless spreading coefficient by means of assuming equilibrium at the very tip ($x = 0$) of the film in spite of an overall non-equilibrium situation: $\Sigma = (2\,S^*/\gamma^*)\,\varepsilon^{-2}$.

The second model corresponds to $A = 0$ (no disjoining pressure), whereas it is reasonable to choose $\mathcal{K} \equiv 1$ given that the Kelvin effect is the key here. Then one uses either $|c| \equiv 1$ or $|E| \equiv 1$, similarly to the first model. At the tip of the film (where $x = 0$ and $\xi = 0$), we now impose a fixed (equilibrium) contact angle $\theta_0 = \varepsilon\,b_0 \ll 1$, where $b_0 = O(1)$ is its rescaled version. In the partial-wetting case ($S^* < 0$, $\Sigma < 0$), according to the Young's law, $b_0 = (-\Sigma)^{1/2}$, where the expression for Σ is formally the same as above. In the perfect-wetting case ($S^* \geq 0$, $\Sigma \geq 0$), we simply take $\theta_0 = 0 = b_0$. Thus, unlike the first model, the second one does not allow discrimination by the value of Σ for $\Sigma > 0$. Using the equation, one can show that the film now starts as $\xi = b_0 x + (E/6\,\mathcal{K})\,x^2 + (b_0^2 c/18\,\mathcal{K})\,x^3 + (b_0 cE/72\mathcal{K}^2)\,x^4 + \cdots$ as $x \to 0$, which remarkably involves no singularities at all, not even integrable. We note that the counterpart of the free coefficient Ω can here be found in a transcendental eigenfunction contribution into the above coordinate expansion.

Finally, let us note that both models need not be limited to their minimalist version. For instance, the first model can incorporate the Kelvin effect and other effects [3] without any "structural" consequences from the viewpoint of the singularity resolution. In fact, such an incorporation of the Kelvin effect permits to establish an interrelation between the truncated regimes studied here and the regimes with extended precursor films considered in the literature [4]. The second model, too, admits the incorporation of the disjoining pressure, provided that the latter remains finite as $\xi \to 0$. In such a case, the micro- contact angle $\theta_0 = \varepsilon\,b_0$ rather corresponds to the augmented Young's one [5].

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References

[1] de Gennes P.G. : Wetting: Statics and Dynamics. *Rev. Mod. Phys.* **57**:827-863, 1985.

[2] Hervet H., de Gennes P.G.: The Dynamics of Wetting: Precursor Films in the Wetting of 'Dry' Solids. *C.R. Acad. Sci. Paris* **299 II**:499-503, 1984.

[3] Colinet P., Rednikov A.Ye.: On Integrable Singularities and Apparent Contact Angles Within a Classical Paradigm. Partial and Complete Wetting Regimes with or without Phase Change. *Eur. Phys. J. – Special Topics* **197**:89-113, 2011.

[4] Rednikov A.Ye., Colinet P.: Truncated versus Extended Microfilms at a Vapor-Liquid Contact Line on a Heated Substrate. *Langmuir* **27**:1758-1769, 2011.

[5] Yeh E.K., Newman J., Radke C.: Equilibrium Configurations of Liquid Droplets on Solid Surfaces under the Influence of Thin-Film Forces. Part I. Thermodynamics. *J. Colloids Surf. A* **156**:137-144, 1999.