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Diffusion-controlled evaporating perfectly wetting meniscus in a channel

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1 Though diffusion-controlled evaporation from capillaries has been studied
2 since the work of Stefan, except for the work of Derjaguin et al. (1965), the
3 interface is treated as a plane surface having known contact angle of 90° .
4 Here, by contrast, the interface location is determined as part of the solution
5 of a free boundary problem coupling hydrodynamic and diffusion fields. We
6 make the following simplifying assumptions. (a) Liquid and vapour at the
7 interface are in local thermodynamic equilibrium; as a result, evaporation is
8 limited by diffusion of the vapour molecules in the gas. (b) The system is

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effectively isothermal; though evaporation induces liquid temperature differences, they are kinetically negligible. Given (a) and (b), the vapour partial pressure is related to the liquid pressure by the Kelvin equation. Though the hydrostatic contact angle is zero, the stationary evaporating meniscus exhibits an apparent contact angle; Θ is determined chiefly by a capillary number $Ca = \mu_\ell V_s / \gamma$ based on surface tension γ , liquid viscosity μ_ℓ , and a velocity scale V_s set by evaporation. Though microphysics must be included in the free boundary problem in order to resolve a hydrodynamic singularity at the contact line, Θ is insensitive to the microphysical details.

1 Introduction

Poulard et al. (2005) have studied experimentally and theoretically the evaporation of a droplet of chemically pure liquid from a perfectly wetted substrate into a mixture of vapour phase with an inert component. For their experimental conditions, evaporation is controlled by steady diffusion within the gas mixture. According to the well-known solution for that diffusion problem, evaporation is concentrated near the apparent contact line. Conservation of mass requires liquid flow towards the contact region, and the pressure differences induced to drive this liquid flow also distort the liquid-gas interface. As a result, the perfectly wetting evaporating system exhibits an apparent contact angle: Θ is a property of the small-scale flow induced by the evaporation, and vanishes (for a perfectly-wetting system) at equilibrium. The authors show that the time evolution of the droplet planform radius can be understood, at least qualitatively, by assuming the droplet to

32 be a spherical cap, and combining a mass balance including evaporative losses
33 with a constitutive equation relating Θ to evaporation rate and to contact
34 line velocity. This constitutive equation was written down using heuristic
35 reasoning.

36 As a first step towards deriving a quantitative expression for the apparent
37 contact angle in that geometry, here we pose and solve completely the free
38 boundary problem describing the evaporating meniscus of a perfectly wetting
39 liquid in a long narrow channel. This geometry offers two advantages over
40 that of the droplet. The meniscus can be kept stationary in an experiment
41 and, provided the capillary number based on the evaporatively-induced liq-
42 uid flow is small, the mathematical problem is one-dimensional. Owing to a
43 separation of lengthscales, its numerical solution is not trivial, however. In
44 order for vapour diffusion from the meniscus to the channel mouth to be ap-
45 proximately one-dimensional, the channel must be long compared with the
46 wall spacing. As a result, the thin wetting films on each wall are also long.
47 As shown by Derjaguin et al.(1965), in very narrow channels, mass transport
48 by liquid flow along these films can be comparable to the axial mass flow by
49 diffusion along the gas column. Our numerical scheme must resolve those
50 large-scale axial features, in addition to the small-scale axial flow occur-
51 ring within the apparent contact region where the apparent contact angle is
52 formed. Using these numerical solutions, we show that the meniscus exhibits
53 an apparent contact angle Θ varying as the cube root of the capillary number
54 based on evaporation rate. (Of course we also predict the evaporation rate
55 as a function of experimentally-controllable parameters.)

2 Boundary Value Problem

Figure 1 shows the geometry of interest: an evaporating meniscus of a completely wetting pure liquid with uniform surface tension γ is formed in the gap between two horizontal flat plates of gap thickness $2a$. The plates are initially at common temperature T_w with the surroundings. The pure liquid evaporates into a binary mixture of its own vapour and an inert component. Evaporation occurs because the vapour partial pressure decreases from its saturation value p_{sat} at the bulk meniscus to ϕp_{sat} at the channel exit; here, ϕ is the relative humidity in the distant gas and p_{sat} the saturation vapour pressure at the uniform temperature T_w of the channel walls. Evaporation draws liquid into the contact region; near the wetted walls, the resulting pressure differences distort the phase interface, creating an apparent contact angle, Θ . We define the origin O at the point where the visible meniscus appears to intersect the lower wall, and define L as the distance from O to the channel exit; to keep the interface fixed relative to the wall, liquid is continuously fed into the channel at the same rate $2\dot{m}$ as it is being evaporated.

Because the liquid is completely wetting, the visible meniscus is preceded by a thin wetting film; we assume that within this thin film, disjoining pressure Π is related to film thickness h_* by $\Pi = A/h_*^3$, where A is the dispersion constant. Together A and γ define a length scale $(A/\gamma)^{1/2}$; this length scale is of molecular dimensions. We assume that the channel gap thickness $2a$ is large compared with the molecular scale; $1 \gg [A/(a^2\gamma)]^{1/2}$. Owing to this separation of scales, the extended meniscus has an inner-and-outer structure: for $\phi = 1$, the system is in hydrostatic equilibrium; for this case, Renket al (1978) showed that the outer visible meniscus is a semicircle of radius

81 a ; the inner solution consists of a non-uniform wetting film in which the
 82 capillary and disjoining pressures are comparable in magnitude. Far from
 83 the apparent contact line, defined by the intersection of the semicircle with
 84 the channel walls, the thickness of the wetting film approaches the uniform
 85 value $(aA/\gamma)^{1/3}$; this thickness is, of course, small compared with a . In this
 86 paper, we analyse the effect of evaporation on that hydrostatic picture.

87 To analyse the evaporating meniscus, we use the separation of scales de-
 88 scribed above. The inner region now consisting of the quasi-parallel liquid
 89 film, and the corresponding portion of the gas column. Within this region,
 90 the lubrication approximation holds within the film and, across the gas col-
 91 umn, the partial pressure is uniform. Owing to these two conditions, the
 92 unknowns depend only on distance along the wall, and the mass transport
 93 within the inner region is determined by problem (1) containing only ordinary
 94 differential equations. For the gas, the outer region is bounded by the visible
 95 circular arc meniscus, and the chord joining the points where that meniscus
 96 intersects the channel walls. Within this region, the vapour partial pressure
 97 p_v^* satisfies the steady diffusion equation subject to the boundary condition
 98 that on the gas-liquid interface, $p_v^* = p_{sat}$, together with the boundary con-
 99 dition that on the chord, p_v^* matches to the solution of the inner problem.

100 We assume that the capillary number $\nu_\ell \dot{m}/a\gamma$ based on liquid kinetic
 101 viscosity ν_ℓ and (half) the evaporation-rate $\dot{m}$ is small compared with unity.
 102 This condition ensures that on the length scale a , the interface remains a
 103 circular arc even in the presence of evaporation. Within the contact region,
 104 however, the pressure differences required to drive liquid towards the region of
 105 maximum evaporation become sufficiently large to distort the phase interface.

106 Within this region, the unknowns $p_v^*(x_*)$, $p_\ell^*(x_*)$, $h_*(x_*)$, and the constant $\dot{m}$
 107 are determined by the following free boundary value problem,

$$\dot{m} = \frac{h_*^3}{3\nu_\ell} \frac{dp_\ell^*}{dx_*} + \frac{aD_v}{R_v T_w} \frac{dp_v^*}{dx_*}, \quad (1a)$$

$$p - p_\ell^* = \gamma \frac{d^2 h_*}{dx_*^2} + \frac{A}{h_*^3}, \quad (1b)$$

$$p_v^* = p_{sat} + \frac{\rho_{sat}}{\rho_\ell} (p_\ell^* - p_b); \quad (1c)$$

$$p_v^*(-L) = \phi p_{sat}, \quad p_v^*(x_* \rightarrow a) \rightarrow p_{sat}, \quad (1d,e)$$

$$h_*(-L) = \left(\frac{A}{p - p_\ell^*} \right)^{\frac{1}{3}}, \quad \frac{d^2 h_*}{dx_*^2} (x_* \rightarrow a) \rightarrow \frac{1}{a} \quad (1f,g)$$

108 where ρ_ℓ is the liquid density, p_b the bulk liquid pressure, p the total pressure
 109 in the gas, R_v the specific gas constant, D_v the binary diffusion coefficient,
 110 and ρ_{sat} the saturation vapour density at T_w . We now interpret (1).

111 Equation (1a) is a statement of mass balance across a cross-section of the
 112 channel. It expresses the mass flow rate $\dot{m}$ due to evaporation in the lower
 113 half of the channel as the sum of the mass flow rates occurring within the
 114 liquid and gas phases. On the right hand side, the first term describes the
 115 mass flow due to a Poiseuille flow within the thin quasi-parallel liquid film;
 116 the second term describes the mass flow by axial diffusion of vapour through
 117 the gas column, and is merely the simplified form of Fick's first law,

$$\dot{m}_x = -\frac{aD_v}{R_v T_w} \frac{dp_v^*}{dx_*}, \quad J^* = \frac{d\dot{m}_x}{dx_*} \quad (2a,b)$$

118 Equation (2) neglects the motion induced within the gas mixture; it is a
 119 good approximation when the saturation vapour pressure is small compared

120 with the total pressure in the gas. The full form of that equation, including
121 induced motion in the gas, is given as equation (28a) in appendix A.3. The
122 mass balance equation (1a) also neglects Marangoni flows; this is a good
123 approximation if the liquid is chemically pure, and temperature differences
124 along the liquid–gas interface are negligibly small.

125 Equation (1b) is a statement of force balance normal to the interface. It
126 states that the pressure force on an interfacial element balances the resultant
127 force due to capillarity and disjoining pressure. On the right hand side, the
128 first term gives the equation of capillarity for a slowly tapered film, whose
129 slope is significantly small compared with unity; the second term describes
130 the disjoining pressure for a uniform film. Here, the adsorption forces are re-
131 stricted to the London-van der Waals dispersion forces. Even though Truong
132 and Wayner (1993) and Levinson et al (1993, figure 3) showed that the in-
133 verse cube dependence for the disjoining pressure is appropriate only for film
134 thicknesses less than $20nm$, we use it here as the effects of disjoining pressure
135 become insignificant for film thicknesses greater than that anyway.

136 Equation (1c) is a simplification of the Hertz-Knudsen equation, see the
137 discussion in appendix A.1. It states that liquid and vapour at the interface
138 are in local thermodynamic equilibrium; as a result, evaporation is controlled
139 by stationary diffusion of the vapour molecules in the gas. Though evapora-
140 tion induces liquid temperature differences, we have assumed that they are
141 kinetically negligible; this approximation is justified in Appendix A.2. In the
142 model of the Stefan diffusion tube described by Bird et al (2006, §18.2), the
143 kinetic equation (1c) is simplified by assuming that liquid pressure differ-
144 ences are negligibly small, even within the contact region where evaporation

145 is strongest. By accounting for liquid pressure differences, equation (1c)
 146 couples the dynamical processes in the liquid to those in the gas phase.

147 Boundary conditions (1e,g) are obtained by matching the outer limit of
 148 the inner solution to the inner limit of the outer solution. Specifically, bound-
 149 ary condition (1g) ensures that the interface curvature at the outer edge of
 150 the inner region matches smoothly to the uniform curvature of the outer
 151 circular arc meniscus; the other boundary condition (1e) is a matching con-
 152 dition on the vapour partial pressure. The vapour pressure at the outer edge
 153 of the inner region is equal to the saturation vapour pressure because for
 154 small capillary number, changes in liquid pressure along the outer meniscus
 155 are negligibly small. Therefore $p_\ell^* = p_b$ to a first approximation, and it follows
 156 from equation (1c) that $p_v^* = p_{sat}$ along the outer circular arc meniscus.

157 Because capillary pressure is negligible within the long tapered wetting
 158 film, boundary condition (1f) on the film thickness at the channel mouth
 159 is obtained by setting surface tension $\gamma = 0$ in equation (1b). This is the
 160 thin film solution described by Derjaguin et al (1965). The other boundary
 161 condition (1d) fixes the vapour pressure at the channel mouth. Unlike the
 162 outer boundary conditions (1e,g), we did not use the asymptotic forms for
 163 the film thickness and liquid pressure along the long tapered film because
 164 that asymptotic solution contains the mass flow $\dot{m}$, which is not known a
 165 priori. According to equation (1g), the film thickness grows parabolically
 166 with distance as $x_* \rightarrow a$; the effects of disjoining pressure are therefore
 167 negligible at the outer edge of the inner region. Consequently, the outer limit
 168 of the stress equation (1b) requires that we chose the constant $p_b = p - \gamma/a$.

169 We non-dimensionalize (1) by letting,

$$\Theta_s = \left(\frac{A}{\gamma a^2} \right)^{\frac{1}{6}}, \quad h_s = a\Theta_s^2, \quad x_s = a\Theta_s \quad (3a-c)$$

170 where h_s and x_s are the characteristic dimensions of the contact region for
 171 hydrostatic state (Renk et al. 1978, equations 2, 10, 21). In the numerical
 172 analysis described in §3, we start with the hydrostatic solution and then use
 173 continuation to obtain solutions for $\phi < 1$; the film thickness scale h_s and
 174 the axial scale x_s are convenient choices for that numerical analysis.

175 We introduce dimensionless variables (without asterisks) by

$$p_\ell = \frac{a}{\gamma}(p_\ell^* - p_b), \quad x = \frac{x_*}{x_s}, \quad h = \frac{h_*}{h_s}. \quad (4a-c)$$

176 To non-dimensionalize (1), we first eliminate the vapour partial pressure in
 177 favour of the liquid pressure using equation (1c); then substituting (4) into
 178 the resulting problem (1), we find that the unknowns h and p_ℓ satisfy the
 179 following dimensionless boundary value problem: for $-\chi/\Theta_s \leq x < \infty$,

$$\frac{d}{dx} \left[\left(\frac{h^3}{3\beta} + 1 \right) \frac{dp_\ell}{dx} \right] = 0, \quad (5a)$$

$$1 - p_\ell = \frac{d^2 h}{dx^2} + \frac{1}{h^3}; \quad (5b)$$

$$p_\ell(-\chi/\Theta_s) = -\alpha, \quad p_\ell(x \rightarrow \infty) \rightarrow 0, \quad (5c,d)$$

$$h(-\chi/\Theta_s) = \left(\frac{1}{1+\alpha} \right)^{\frac{1}{3}}, \quad h(x \rightarrow \infty) \rightarrow \frac{x^2}{2} \quad (5e,f)$$

180 We have differentiated equation (1a) once so as to eliminate the integration
 181 constant $\dot{m}$. Boundary conditions (5d,f) are applied at infinity because the

182 slope unit $\Theta_s \ll 1$ owing to the separation of length scales described at
 183 the beginning of this section. However, boundary conditions (5c,e) are not
 184 applied at minus infinity because for $x < 0$, the solution continues to depend
 185 upon χ through the length of the gas column. Matching condition (1g) on
 186 the interface curvature far from the apparent contact line has been integrated
 187 and replaced with its asymptotic form (5f). Because the independent variable
 188 now appears explicitly in that boundary condition, the problem is no longer
 189 autonomous; as a result, the origin is fixed at the apparent contact line and
 190 can no longer be arbitrarily chosen. Four independent parameters appear in
 191 the dimensionless boundary value problem, namely; α , β , χ , and Θ_s .

$$\alpha = \frac{a\rho_\ell}{\gamma\rho_{sat}}p_{sat}(1 - \phi), \quad \beta = \frac{\nu_\ell\rho_{sat}\gamma D_v}{\rho_\ell R_v T_w A}, \quad \chi = \frac{L}{a} \quad (6a-c)$$

192 According to equations (1c, d, e), the liquid pressure decreases from p_b at the
 193 bulk meniscus to $p_b - \rho_\ell p_{sat}(1 - \phi)/\rho_{sat}$ at the channel mouth; α is the ratio
 194 of the pressure-difference $\rho_\ell p_{sat}(1 - \phi)/\rho_{sat}$ driving the resulting flow to the
 195 pressure-difference γ/a across the bulk meniscus. For fixed α and position
 196 x , the parameter β controls the fraction of the total mass flow transported
 197 by axial diffusion in the gas. The parameter χ is the channel's aspect ratio.

198 For use in subsequent analysis, we define

$$f = \frac{\dot{m}}{\dot{m}_s} \quad \text{where} \quad \dot{m}_s = \frac{aD_v p_{sat}}{R_v T_w L}(1 - \phi) \quad (7a,b)$$

199 According to the simplified form of Fick's law, $\dot{m}_s$ is the diffusive transport
 200 caused by a gradient $(1 - \phi)p_{sat}/L$ of vapour concentration. The integration
 201 constant f is the ratio of the total evaporation from the capillary to $\dot{m}_s$.

Table 1 shows representative values for the parameters in the theory. We have used $A = 10^{-21}J$ for the dispersion constant, $a = 10\mu m$ for capillary radius, and $\phi = 0.3$ for the relative humidity in the distant gas. All material properties are evaluated at the uniform wall temperature $T_w = 298K$. The slope unit Θ_s is small as expected whereas α is generally large, except when the system is near hydrostatic equilibrium. In general, $0.01 < \beta < 1$.

3 Numerical Method

The governing equations (5) are numerically solved using the NAG routine D02TKF, which uses the collocation method to approximate the solution at certain specified locations within the problem domain; solution values anywhere else within the problem domain are obtained using polynomial interpolation. The routine uses variable steps in x with deferred correction. The codes and numerical scheme are discussed at length in Njante (2012).

We use the finite domain size $x = [-\chi/\Theta_s, 1/\Theta_s]$ for the computation. Since the slope unit $\Theta_s \ll 1$, we solve for $\Theta_s \rightarrow 0$; and for $\alpha \rightarrow \infty$ because then a contact angle is established. These limiting solutions complicate the analysis for the following two reasons: first, the resulting system of non-linear algebraic equations, for the coefficients of the basis functions, becomes very ill-conditioned as $\alpha \rightarrow \infty$; secondly, the problem domain becomes infinite in the limit as $\Theta_s \rightarrow 0$. This work alleviates both difficulties by using continuation in the parameters α and Θ_s . Specifically, numerical solutions are first obtained for the hydrostatic case $\alpha = 0$ and $\Theta_s > 0$ using the initial approximations; $p = 0$ and $h = 1$. The obtained solutions are then used as initial

225 guesses in the solution for $\alpha = \alpha + \Delta\alpha$ and $\Theta_s = \Theta_s - \Delta\Theta_s$. The process
 226 is repeated until we obtain solutions for the values α and Θ_s that we desire.
 227 If the value of Θ_s is not too small, then continuation in Θ_s is unnecessary.
 228 For a desired value of $\Theta_s \rightarrow 0$, continuation must be used in order to avoid a
 229 possible numerical singularity in the Jacobian used in the Newton iteration.

230 Figure 2 compares the numerical solution of problem (5) without approx-
 231 imation with the analytic solution obtained by neglecting capillarity in the
 232 differential equations (Njante 2012, equation 3.2). Within the long slowly
 233 tapered section of the meniscus, capillarity is negligible. This explains the
 234 good agreement between the two solutions in that part of the meniscus. The
 235 agreement confirms the robustness and accuracy of our numerical scheme.

236 In the thermal model, DasGupta et al (1993) integrated the corresponding
 237 equations using the shooting method. This problem differs from the thermal
 238 problem because the solution continues to depend on both constants in the
 239 starting series. It is for this reason that we decided to solve the problem
 240 as a boundary value problem. One consequence of solving the problem as a
 241 boundary value problem is that the contact angle cannot be directly obtained
 242 from the model problem using a local analysis around the contact region;
 243 unless the constant k described in §4 is obtained using an iterative process.
 244 It is for this reason that we scale the problem, making sure that the interface
 245 curvature does not vanish at the outer edge of the problem domain. Once
 246 the numerical solutions are obtained on these set of scales, the contact angle
 247 can then be extracted from the computed values of h as explained in §5.

248 4 Rescaling the equations

249 By its definition, the apparent contact angle $\Theta = b\Theta_s$, where the proportion-
 250 ality constant b is obtained by solving problem (5). Because the solution to
 251 problem (5) is a function of the parameters α, β, χ and Θ_s , so is the propor-
 252 tionality constant: $b = b(\alpha, \beta, \chi, \Theta_s)$. Though problem (5) is conveniently
 253 solved numerically, obtaining a correlation between b and the control param-
 254 eters is non-trivial. For this work, dimensional analysis is used to obtain a
 255 correlation between b and the control parameters $\alpha, \beta, \chi, \Theta_s$. The correlation
 256 coefficient is obtained by comparing the result from dimensional analysis to
 257 the numerical solution to problem (5). To begin, we rescale (1) by letting

$$\eta_s = \left(\frac{\nu_\ell a D_v \rho_{sat}}{R_v T_w \rho_\ell} \right)^{\frac{1}{3}}, \quad \xi_s = \left(\frac{\gamma \rho_{sat} L \eta_s}{\rho_\ell p_{sat} (1 - \phi)} \right)^{\frac{1}{3}} \quad (8a-c)$$

258 The thickness scale η_s is the film thickness at which diffusion along the gas
 259 column balances liquid flow along the film. The length ξ_s is the axial scale
 260 at which Poiseuille flow driven by gradient in capillary pressure balances
 261 the mass loss from the capillary. By their definition, both length scales are
 262 independent of the dispersion constant A . The axial scale ξ_s is a decreasing
 263 function of the potential difference $p_{sat}(1 - \phi)$ driving the evaporation.

264 Table 2 shows estimates for the film thickness scale η_s and axial length
 265 scale ξ_s for different channel sizes. We have used $A = 10^{-21} J$ for the dis-
 266 persion constant, $L = 5a$ for the film length, and $\phi = 0.3$ for the relative
 267 humidity in the distant gas. Material properties are evaluated at the uniform
 268 wall temperature $T_w = 298K$. The material considered is water. As can be
 269 seen from the table, the axial scale $\xi_s \ll a$ and the apparent contact angle,

270 which is proportional to the slope unit η_s/ξ_s , is about a tenth of a radian.

271 We now define new variables by

$$\eta = \frac{h_*}{\eta_s}, \quad \xi = \frac{x_*}{\xi_s} \quad (9a,b)$$

272 Substituting these new variables into problem (1), we find that the interface
273 shape η satisfies the following boundary value problem: for $-\infty < \xi < \infty$,

$$\left[\frac{\eta^3}{3} + 1 \right] \left[\frac{3\beta}{\sigma\eta^4} \frac{d\eta}{d\xi} - \frac{d^3\eta}{d\xi^3} \right] = f; \quad (10a)$$

$$as \quad \xi \rightarrow \infty : \quad \frac{d^2\eta}{d\xi^2} \rightarrow \frac{1}{\sigma} \quad (10b)$$

$$as \quad \xi \rightarrow -\infty : \quad \eta \rightarrow \left(\frac{\beta}{c - \sigma f \xi} \right)^{\frac{1}{3}} \quad (10c)$$

274 The domain is the real line because $\xi_s \ll a$ as shown in Table 2. According
275 to the mass balance equation (1a), for $h_* \ll \eta_s$, transport is by diffusion
276 along the gas column; boundary condition (10c) on the film thickness at
277 minus infinity is therefore obtained by neglecting both capillarity and film
278 transfer in equation (10a). The integration constant c is obtained by match-
279 ing the thin film solution (10c) to the film thickness at the channel exit. At
280 the channel exit, $\xi = -L/\xi_s$ and $\eta^3 = 1/\beta(1+\alpha)$, so that $c = \beta^2(1+\alpha) - \alpha f$.

281 The pressure ratio

$$\sigma = \left(\frac{\alpha}{\chi} \Theta_s \beta^{1/6} \right)^{2/3} \quad (11)$$

282 compares the pressure jump $\gamma\eta_s/\xi_s^2$ across the interface within the region
283 where evaporation is maximised to the pressure jump γ/a across the interface

284 at infinity. A contact angle is thus formed if $\sigma \gg 1$. To verify this result,
 285 we apply the limit $\sigma \rightarrow \infty$ to equations (10) to show that η satisfies

$$\left[\frac{\eta^3}{3} + 1 \right] \frac{d^3 \eta}{d\xi^3} = -f; \quad \text{with} \quad \frac{d^2 \eta}{d\xi^2} \rightarrow 0 \quad \text{as} \quad \xi \rightarrow \infty, \quad (12a,b)$$

286 and a matching condition at $-\infty$, to be explained. According to the inner
 287 problem (10), the film thickness grows parabolically with distance as $\xi \rightarrow \infty$.
 288 This parabolic growth is necessary for matching the inner solution to the
 289 circular arc meniscus described in §2. The limit $\sigma \rightarrow \infty$ is singular for two
 290 reasons: first, disjoining pressure is negligible; an inner region Ia is therefore
 291 necessary to satisfy the thin film boundary conditions. Secondly, because
 292 the interface curvature vanishes at ∞ , according to (12b), the film thickness
 293 grows linearly with distance as $\xi \rightarrow \infty$; as a result, problem (12) does not
 294 describe the parabolic arc meniscus. An outer region Ic is therefore necessary;
 295 otherwise, matching to the circular arc meniscus will be impossible. The two
 296 regions, i.e Ia and Ic, are connected together by an intermediate region Ib.
 297 We integrate the intermediate problem (12) to show that for $\xi \rightarrow \infty$,

$$\frac{d\eta}{d\xi} = k - \frac{3f}{2k^3} \xi^{-1} + o(1), \quad p = -\frac{3f}{2k^3} \xi^{-2} + o(1) \quad (13a,b)$$

298 where k is an integration constant. Equation (13b) shows that the the vapour
 299 pressure asymptotically approaches the saturation pressure at the outer edge
 300 of the intermediate region; as a result, the vapour pressure is asymptotically
 301 equal to the saturation pressure throughout the entire region described by
 302 the parabolic arc meniscus; evaporation from the parabolic arc meniscus is
 303 therefore asymptotically negligible. All the evaporation thus occurs within

sub-regions Ia and Ib. However, as concluded by Njante(2012, equation 3.4), for $\alpha \rightarrow \infty$, evaporation from the precursor film is negligible; as a result, the intermediate region Ib determines the total evaporation from the capillary.

Equation (13a) shows that the apparent contact angle is well defined. The correction term of $O(\xi^{-1})$ is included to stress that the slope approaches a limit at infinity. The stationary evaporating meniscus thus differs from the moving isothermal meniscus. The dynamic contact angle in that problem is poorly-defined: though the curvature vanishes at infinity, the slope there continues to grow as $(\ln \xi)^{1/3}$ (see de Gennes 1985, Equation 4.29). The slope thus depends weakly on position x whereas in the present case, it approaches a limit at infinity. Because the slope approaches a limit at the outer edge of the intermediate region, an apparent contact angle Θ is established there. Specifically, $\Theta = (\eta_s/\xi_s)k$. Comparing with $\Theta = b\Theta_s$, we find that

$$b = k\beta^{1/6}\sqrt{\sigma} \quad \text{where} \quad k = \lim_{\sigma \rightarrow \infty} \lim_{\eta \rightarrow \infty} \left(\frac{d\eta}{d\xi} \right). \quad (14a,b)$$

We have used equations (3a,6) to express $\eta_s/\xi_s\Theta_s$ as a function of the control parameters. By (14b), a contact angle is established for $\sigma \rightarrow \infty$. However, because $\Theta \sim \eta_s/\xi_s$, the expression for Θ does not contain a/ξ_s . Consequently, the contact angle Θ can be of order unity, even though $\sigma = a\eta_s/\xi_s^2 \gg 1$.

5 Obtaining b numerically

According to boundary condition (1f), the interface curvature approaches a constant at the outer edge of region I; the film thickness thus grows parabolically with distance as $x \rightarrow \infty$. If the parabola so defined has a zero, then a

325 contact angle is defined by the slope at $h = 0$. Since the entire interface does
 326 not have a constant curvature, an apparent contact angle is defined by first
 327 computing the constant curvature profile for large h , and then extrapolate
 328 down to $h = 0$. To give a precise definition of Θ using this method, we multi-
 329 ply the asymptotic relation $d^2h/dx^2 \sim 1$ by $2dh/dx$, and then integrate once
 330 in x to show that $(dh/dx)^2 \sim 2h + b^2$, where b^2 is the integration constant.
 331 We therefore use the definition $\Theta = b\Theta_s$, where the integration constant

$$b^2 = \lim_{\sigma \rightarrow \infty} \lim_{h \rightarrow \infty} \left[\left(\frac{dh}{dx} \right)^2 - 2h \right] \quad (15)$$

332 According to boundary value problem (5), for $\alpha = 0$, the system is in hy-
 333 drostatic equilibrium; for $\alpha > 0$, the liquid pressure at the channel exit is
 334 less than the bulk liquid pressure. As a result, liquid flows from the bulk
 335 meniscus into the contact region; σ is proportional to the pressure gradient
 336 driving that flow. The limit $\sigma \rightarrow \infty$ in equation (15) therefore ensures that
 337 the liquid motion is strong enough to distort the liquid-gas interface and
 338 also to create an apparent contact angle Θ . The other limit $h \rightarrow \infty$ picks
 339 out the constant curvature part of the phase interface, and also ensures that
 340 the apparent contact angle defined by equation (15) is independent of film
 341 thickness. Numerical solutions are now used to establish the existence of Θ .

342 Figure 3 shows the interface curvature d^2h/dx^2 computed without ap-
 343 proximation from the inner problem (5) as a function of film thickness h ;
 344 on the right hand side of the figure, $d^2h/dx^2 \rightarrow 1$, as required by boundary
 345 condition (5f). Near the origin, however, $d^2h/dx^2 \rightarrow 1$ has a local maximum
 346 for 3 of the 4 curves. The maximum value is an increasing function of the
 347 potential difference $p_{sat}(1 - \phi)$ driving evaporation. For $\phi = 1$, the system is

348 in hydrostatic equilibrium; for $\phi < 1$, the partial pressure at the channel exit
 349 is less than the value required for the liquid to coexist in equilibrium with
 350 its vapour, and as a result, liquid evaporates from the extended meniscus.
 351 This explains why the interface shape is not perturbed for $\sigma \rightarrow 0$, bottom
 352 curve. For $\sigma \rightarrow \infty$ however, the flow becomes strong enough to perturb the
 353 interface, and as a result, creates an apparent contact angle, see the top three
 354 curves. Figure 3 therefore supports the limit define in equation (15).

355 Figure 4 shows the squared interface slope $(dh/dx)^2$ computed from the
 356 inner problem (5) without approximation as a function of film thickness h ;
 357 as expected, $(dh/dx)^2$ is an increasing function of the potential difference
 358 driving evaporation. On the right hand side of the figure, $(dh/dx)^2$ grows
 359 linearly with h ; this linear growth marks the constant curvature portion of
 360 the phase interface. The limit $h \rightarrow \infty$ in equation (15) thus picks out the
 361 constant curvature part of the phase interface as claimed earlier. As can be
 362 seen from the graphs, the interface curvature becomes uniform only for film
 363 thicknesses $h > 10$. Therefore to extract b from the computed values of h ,
 364 we first discard all data for $h < 10$, and then fits a straight line to the rest
 365 using the least square method. The intercept of that line determines b^2 .

366 **6 Computation of k**

367 Computing k directly from (10) requires significant computing power. For
 368 this reason, we find k by comparing the scaling relation (14) to the numerical
 369 solution for b obtained in the previous section. To begin, we note that because
 370 the solution to (10) depends on σ and β , so is the integration constant k .

371 Consequently, for $\sigma \rightarrow \infty$, the constant k is a function of β alone. Therefore
 372 keeping β fixed, equation (14) predicts that a plot of b against $\beta^{1/6}\sqrt{\sigma}$ should
 373 give a straight line, whose slope k depends on the size of β alone.

374 Figure 5 shows the integration constant b computed from (5) using the
 375 method described in §5 as a function of $\beta^{1/6}\sqrt{\sigma}$. As expected, b is a linear
 376 function of $\beta^{1/6}\sqrt{\sigma}$; the slope k of each line is a function of β . The very
 377 small scatter in the numerical solutions is a clear indication that k is a very
 378 weak function of β . Armed with this information, we plot b as a function of
 379 the parameter $\beta^\delta\beta^{1/6}\sqrt{\sigma}$, where the exponent $\delta \ll 1$ is chosen, by trial and
 380 error, so as to collapse the numerical solutions onto a single straight line.

381 Figure 6 shows that the choice $\delta = 4/225$ collapses the numerical solutions
 382 onto a single straight line as $\beta^\delta\beta^{1/6}\sqrt{\sigma} \rightarrow \infty$; this implies that the slope
 383 parameter $b \rightarrow s\beta^\delta\beta^{1/6}\sqrt{\sigma}$ as $\beta^\delta\beta^{1/6}\sqrt{\sigma} \rightarrow \infty$, where s is the slope of the line.
 384 The figure shows that the numerical solutions collapse onto the straight line
 385 only for values of $\beta^\delta\beta^{1/6}\sqrt{\sigma} > 3$. Therefore, to obtain s from the numerical
 386 solutions, we first discard all data for $\beta^\delta\beta^{1/6}\sqrt{\sigma} < 3$, and then fits a line to
 387 the rest using the least square method. The slope of that line determines s .
 388 Using this method, we find that $s \simeq 1.76$. The related expression for b is

$$b = 1.76\beta^{4/225}\beta^{1/6}\sqrt{\sigma} \quad as \quad \sigma \rightarrow \infty \quad (16)$$

389 Equation (16) provides a useful correlation between b , σ , and β . Comparing
 390 this result to the scaling relation (14), we find that $k = 1.76\beta^{4/225}$, which
 391 is a very weak function of β as suggested in figure 5. The corresponding
 392 expression for the apparent contact angle, $\Theta = (\eta_s/\xi_s)k$, is given by

$$\Theta = kCa^{1/3} \quad \text{where} \quad Ca = \frac{\nu_\ell \dot{m}_s}{\gamma \eta_s} \quad (17a,b)$$

393 We have used equation (8) for η_s/ξ_s and the definition $Ca = \mu_\ell V_s/\gamma$ for a
 394 capillary number based on a velocity scale $V_s = \dot{m}_s/\rho_\ell \eta_s$ set by evaporation.
 395 By its definition, Ca is independent on the dispersion constant A ; and as a
 396 result, micro-physics affects Θ only through the integration constant k . We
 397 recall that $k = 1.76\beta^{4/225}$ is a function of the dispersion constant through β .

398 Figure 7 shows k as a function of β . The graph shows that the contact
 399 angle depends very weakly on micro-physics, except for $\beta \rightarrow 0$. Physically,
 400 the film thickness at which the contact angle is established is proportional
 401 to the parameter $\beta^{1/3}$. Therefore for $\beta \rightarrow 0$, the contact angle is established
 402 at the scale where disjoining pressure is significant. This also explains why
 403 the contact angle varies weakly with β for large β ; here, Θ is established at
 404 a scale where disjoining pressure is insignificant. These effects can also be
 405 explained by first noting that β measures the viscous resistance to liquid flow;
 406 which implies that for large β , liquid motion, and hence the distortion of the
 407 interface, occurs at a much larger scale than that at which disjoining pressure
 408 is significant. Figure 7 covers a sufficiently wide range of β , including the
 409 range typical in applications. Specifically, it covers $10^{-3} \leq \beta \leq 10^3$, and the
 410 figure shows that over this range of β , the integration constant

$$1.5 < k < 2.0 \quad \text{so that} \quad \Theta = 1.75Ca^{1/3} \quad (18a,b)$$

411 with very little error. Equation (18b) expresses the apparent contact angle
 412 as a function of a single parameter Ca depending only on well-known macro-

413 physical properties. Though micro-physics must be included in the boundary
 414 value problem in order to resolve a hydrodynamic singularity at the contact
 415 line, Θ is insensitive to the microphysical details. The insensitivity of Θ to
 416 the value of the dispersion constant has been obtained before for the thermal
 417 problem by Stephan and Busse (1992) and by Morris (2001). In agreement
 418 with the heuristic argument of Poulard et al (2005, Equation 14), Θ varies
 419 as the one-third power of a capillary number based on the evaporation rate.

420 Unlike the thermal problem, the apparent contact angle for a diffusion
 421 controlled evaporating meniscus is a function of the capillary size. To explain
 422 why, we first note that the contact angle increases with the evaporation rate,
 423 irrespective of the boundary condition driving the evaporation. In the case
 424 of a diffusion-controlled evaporating system however, the rate of evaporation
 425 is proportional to the capillary radius. This explains why the contact angle
 426 here increases with the outer length scale. In the thermal problem, the outer
 427 length scale enters the problem only through an outer boundary condition
 428 describing the bulk meniscus. Because a local analysis around the contact
 429 region does not include that outer boundary condition, the apparent contact
 430 angle for the thermal problem is independent on the outer length scale.

431 **7 Conclusion**

432 To analyse the evaporating meniscus, we have used the separation of scales
 433 described in §2. The inner region consists of a quasi-parallel liquid film, and
 434 the corresponding portion of the gas column. Within this region, the lubri-
 435 cation approximation holds within the film and, across the gas column, the

436 partial pressure of the vapour is uniform. Owing to these two conditions, the
 437 unknowns depend only on distance along the wall, and the mass transport
 438 within the inner region is determined by boundary value problem (1) con-
 439 taining only ordinary differential equations. For the gas, the outer region is
 440 bounded by the visible circular arc meniscus, above which the vapour partial
 441 pressure p_v^* is asymptotically equal to the saturation pressure throughout the
 442 entire region. The first conclusion of this work is that the liquid and vapour
 443 flow is completely determined by the solution of the inner problem (1).

444 Poulard et al (2005) have shown experimentally that the diffusion con-
 445 trolled meniscus of a perfectly wetting system exhibits an apparent contact
 446 angle; Θ vanishes when the system is in hydrostatic equilibrium, and is an
 447 increasing function of the potential difference $(1 - \phi)p_{sat}$ driving evapora-
 448 tion. For the first time, we have posed and solved a boundary value problem
 449 whose solution exhibits an apparent contact angle. We give the condition un-
 450 der which the apparent contact angle will be observed; as Figure 3, we give
 451 numerical results demonstrating this condition. As equation (16), we give a
 452 scaling law describing the dependence of Θ on the control parameters in the
 453 theory. Lastly, as equation (18b) we give an explicit formula for Θ as a func-
 454 tion of a capillary number Ca , depending only on well-known macro-physical
 455 properties; even though microphysics must be included in the boundary value
 456 problem in order to resolve a hydrodynamic singularity at the contact line,
 457 the apparent contact angle Θ is insensitive to the microphysical details.

458 **A Derivation of the Governing Equations**

459 **A.1 Conditions Under Which The Simplified Kinetic** 460 **Equation (1c) Holds**

461 Let $\mathcal{P}(T, p_\ell^*)$ be the local co-existence pressure; i.e the vapor pressure required
462 for liquid and vapor to co-exist at temperature T and pressure p_ℓ^* . Then
463 by kinetic theory, $CJ^*/\lambda = (\mathcal{P} - p_v^*)$, see Cammenga (1980). Liquid thus
464 evaporates at any point along the interface if the vapor pressure on the gas
465 side of the interface is less than the co-existence pressure. Also, let p_o be the
466 vapor pressure at the exit of the channel, and T_o the temperature at which
467 liquid and vapor co-exist when both are at pressure p_o . Then following Morris
468 (2000), the kinetic equation is simplified by expanding $(\mathcal{P} - p_v^*)$ in a Taylor
469 series about the reference state (p_o, T_o) . To a first order approximation,

$$\frac{CJ^*}{\lambda} = \frac{\rho_s Q}{T_o} (T - T_o) + \frac{\rho_s}{\rho_\ell} (p_\ell^* - p_o) - (p_v^* - p_o) \quad (19)$$

470 where ρ_ℓ is the liquid density, Q the latent heat of vaporization, C the speed of
471 sound in the gas, $\lambda = \sqrt{2\sigma/\pi}$ a kinetic constant, σ the specific heat ratio, and
472 ρ_s the saturation vapour density at temperature T_o . In the thicker portions
473 of the meniscus, i.e on the scale of the channel gap thickness, diffusion is
474 rate limiting; as a result, the term on the left of (19) vanishes far from the
475 contact line. Hence, we apply the condition that $J \rightarrow 0$ at infinity to obtain

$$0 = \frac{\rho_s Q}{T_o} (T_w - T_o) + \frac{\rho_s}{\rho_\ell} (p_b - p_o) - (p_s - p_o) \quad (20)$$

476 where far from the wall, the interface temperature is assumed to be equal to
 477 the wall temperature; evaporative cooling is therefore taken as negligible at
 478 infinity. p_s is the saturation pressure at temperature T_o . Equation 20 gives
 479 T_o as a function of the boundary values p_b , p_s , p_o , and T_w which are all given
 480 as part of the solution. By subtracting equation 20 from 19, we obtain

$$\frac{C J^*}{\lambda} = \frac{\rho_s Q}{T_o} (T - T_w) + \frac{\rho_s}{\rho_\ell} (p_\ell^* - p_b) - (p_v^* - p_s) \quad (21)$$

481 In equation 21, T_o can be replaced by T_w because $|T_w - T_o| \ll T_o$ in appli-
 482 cations. We have therefore eliminate T_o and p_o in favour of known boundary
 483 values. Because there is no build up of mass at the interface, specie mass bal-
 484 ance there requires that the rate of transfer of molecules across the interface
 485 be equal to the diffusion flux evaluated at the interface. Specifically

$$-\Lambda \frac{\partial p_v^*}{\partial n} = \frac{\rho_s Q}{T_w} (T - T_w) + \frac{\rho_s}{\rho_\ell} (p_\ell^* - p_b) - (p_v^* - p_s) \quad (22)$$

486 where $\Lambda = CD_v/\lambda R_v T_w$ is the mean free path of the vapor molecules in
 487 the gas. The mixed boundary condition (22) couples the dynamical pro-
 488 cesses in the surrounding gas to those in the liquid phase. This coupling of
 489 the different physics make direct analysis difficult. We therefore make the
 490 following simplifying assumptions: (i) The continuum approximation holds
 491 within the surrounding gas; as a result, liquid and vapor at the interface are
 492 in local thermodynamic equilibrium. (ii) The system is effectively isother-
 493 mal; though evaporation induces liquid temperature differences, they are
 494 kinetically negligible for the slow evaporation processes considered here.

495 Given (i) and (ii), equation 22 simplifies to

$$p_v^* = p_s + \frac{\rho_s}{\rho}(p_\ell^* - p_b) \quad (23)$$

496 A.2 Conditions for Isothermal Evaporation

497 The latent heat consumption caused by evaporation at the interface induces
 498 temperature gradients within the drop, substrate, and surrounding gas. One
 499 can estimate the order of magnitude for temperature differences within the
 500 drop by making use of the energy balance $\kappa \nabla T \cdot n_1 = QJ^*$ at the interface,
 501 where κ is the liquid thermal conductivity, n_1 the unit normal to the interface
 502 with the other parameters defined above. The energy balance states that all
 503 heat conducted from the wall to the interface is absorbed as latent heat.
 504 Because there is no build up of mass at the interface, the evaporative flux
 505 term J is estimated using Fick's law $J = D_v \nabla c \cdot n_2$, where n_2 is the unit
 506 normal at the interface into the gas and $c = p_v^*/R_v T_w$. Eliminating J between
 507 the two equations, Fick's law and energy balance, we find that at the interface

$$\kappa \frac{\partial T}{\partial n_1} = \frac{Q D_v}{R_v T_w} \frac{\partial p_v^*}{\partial n_2} \quad (24)$$

508 To a first approximation, the vapour flow occurs in a half-space and so has
 509 just one length scale δ/Θ , where δ is a characteristic film thickness. Near
 510 the contact line, where temperature differences across the drop are highest,
 511 the liquid flow occurs in a wedge of contact angle Θ , and so has two length
 512 scales δ/Θ and δ . Then, according to equation 24, we estimate that

$$\Delta T \sim \Theta \frac{Q D_v}{\kappa R_v T_w} p_s (1 - \phi) \quad (25)$$

where p_s is the saturation vapour pressure, ϕ the relative humidity in the distant gas, and ΔT the characteristic temperature difference across the drop. According to equation 22, temperature differences within the drop are kinetically negligible if the first term on the right is negligibly small as compared to the third term; i.e if $\rho_s Q \Delta T / T_w \ll p_s (1 - \phi)$, which translates to

$$\epsilon = \frac{\rho_s Q^2 D_v \Theta}{\kappa R_v T_w^2} \ll 1 \quad (26)$$

Both ϵ and ΔT depend on the drop size through Θ . The parameter ϵ is given in Sultan et al (2005, row 7, table 2) as the ratio of a thermal expansion number to a kinetic Peclet number; in their notation $\epsilon = \chi / Pe_k$.

In table 3, we give some estimates for the parameters. Values of Θ for the first two rows are taken from Cachile et al (2002); the last row from Deegan et al (2000). The relative humidity $\phi = 0$ for the organic liquids and $\phi = 0.4$ for water. The table shows that temperature gradients, and hence Marangoni flows, become increasingly significant as the drop thickness increases; i.e for drops with large Θ . This does not mean that heat conduction becomes the controlling mechanism because for that to happen, the drop size must be small compared with the mean free path Λ of the vapour in the gas.

A.3 Derivation of Equation (1a)

To simplify the problem, we assume that transport of the vapour molecules in the gas is by axial diffusion only; though there are concentration gradients in

the radial direction, they are negligibly small in the limit $a/L \rightarrow 0$. Balancing mass on the differential control volume in figure ??a requires that

$$\dot{m}_x + \dot{m}_g - \dot{m}_{x+dx} = \frac{d}{dt}m_{sys} \quad (27)$$

Where $\dot{m}_x$ is the rate at which mass is entering the control volume, $\dot{m}_g$ the rate at which mass is generated within the control volume, $\dot{m}_{x+dx}$ the rate at which mass is leaving the control volume, and m_{sys} the total mass within the control volume at any given instant. These quantities are given as

$$\dot{m}_x = \frac{D_v p}{R_v T_w} A_c(x) \frac{d}{dx} \ln \left(1 - \frac{p_v}{p} \right) \quad (28a)$$

$$\dot{m}_g = J(x) dA_s \quad (28b)$$

$$\dot{m}_{x+dx} = \dot{m}_x + \frac{d\dot{m}_x}{dx} dx \quad (28c)$$

Where $A_c(x)$ is the cross-sectional area of the channel, dA_s the surface area of the differential element, $p_v(x)$ the vapour pressure, $J(x)$ the evaporative mass flux normal to the interface, p the total gas pressure, D_v the binary diffusion coefficient, R_v the specific gas constant, and T_w the wall temperature. Equation 28a expresses Fick's first law; it assumes that the medium into which evaporation occurs is stationary, and that the gas mixture is ideal. Taylor expanding equation 28a gives us 28c. For a channel made up of two parallel plates, $A_c(x) = a - h(x)$ and $dA_s = dx$ per unit depth of channel. Due to symmetry, we have considered only the lower half of the channel. Under steady state conditions, equations 27 and 28 gives

$$J = \frac{D_v p}{R_v T_w} \frac{d}{dx} \left[(a - h) \frac{d}{dx} \ln \left(1 - \frac{p_v}{p} \right) \right] \quad (29)$$

548 Using lubrication theory, the mass flow rate in the thin quasi-parallel liquid
 549 film is related to the local evaporative mass flux J by

$$\frac{d}{dx} \left[\frac{h^3}{3\nu} \frac{dp_\ell}{dx} \right] = J \quad (30)$$

550 Equation (30) neglects shear stress at the interface. We now eliminate J
 551 between equations (29) and (30); then integrate once to show that

$$\frac{h^3}{3\nu} \frac{dp_\ell}{dx} - \frac{D_v p}{R_v T_w} (a - h) \frac{d}{dx} \ln \left(1 - \frac{p_v}{p} \right) = -\dot{m} \quad (31)$$

552 For $p_v/p \rightarrow 0$ and for $h \ll a$, equation (31) reduces to (1a).

Liquid	$10^{-4}\alpha$	β	Θ_s
<i>Heptane</i>	0.5529	0.2072	0.0282
<i>Octane</i>	0.4550	0.3107	0.0277
<i>Water</i>	1.3280	0.2113	0.0228

Table 1: Estimates of parameters

$a(\mu m)$	$\eta_s(nm)$	$\xi_s(nm)$	η_s/ξ_s	$10^{-3}a/\xi_s$
10	12	76	0.154	0.13
1000	55	590	0.093	1.69

Table 2: Characteristic dimensions of the contact region

<i>Liquid</i>	$\Theta(rad)$	$\Delta T(K)$	ϵ
Octane ²	0.015	0.10	0.007
Heptane ²	0.030	0.23	0.011
Water ⁵	0.26	15.62	1.56

Table 3: Estimates for ΔT and ϵ

Figure 1: The evaporating meniscus in a channel as seen on the scale of the channel gap thickness $2a$. The origin is at point O , with the positive x -axis to the right.

Figure 2: Liquid pressure $(p_\ell^* - p_b)a/\gamma$ as a function of position x^*/a : open circles, analytic solution obtained from problem (5) by neglecting the first term on the right of equation (5b); solid curve, computed without approximation from (5). With $\chi = 3$, $\alpha = 10$, $\beta = 0.2$, and $\Theta_s = 0.01$: for χ , α , β , and Θ_s , see (6) and (3) respectively.

Figure 3: Interface curvature $a(d^2h^*/dx^{*2})$ computed without approximation from the inner problem (5) as a function of film thickness $h = h^*/h_s$. The curves represent values computed for: A, $\sigma = 10$; B, $\sigma = 6$; C, $\sigma = 4$; D, $\sigma = 0.5$. The length scale h_s is defined in equation (3) while the parameters β and σ are defined in equations (6,11).

Figure 4: Squared interface slope $(\gamma a^2/A)^{1/3}(dh^*/dx^*)^2$ computed without approximation from the inner problem (5) as a function of film thickness $(\gamma/aA)^{1/3}h^*$. Broken curves represent values computed for: A, $\sigma = 10$; B, $\sigma = 6$; C, $\sigma = 4$. These are the same values used in computing figure 3. The solid line represents a line fit for large h , using the least square method. See definitions (11,6) for the parameters σ and β respectively.

Figure 5: Slope parameter b as a function of the parameter $\beta^{1/6}\sqrt{\sigma}$: Symbols denote values computed without approximation from problem (5) using the definition (15) of b : Triangles, $\beta = 10$; open circles, $\beta = 0.1$; plus sign, $\beta = 1$; and squares for selected values of β between 0.01 and 30. These values include the range typical in applications.

Figure 6: Slope parameter b as a function of the parameter $\beta^{4/225}\beta^{1/6}\sqrt{\sigma}$: Symbols denote values computed without approximation from problem (5) using the definition (15) of b : Triangles, $\beta = 10$; open circles, $\beta = 0.1$; plus sign, $\beta = 1$; and squares for selected values of β between 0.01 and 30. These values include the range typical in applications.

Figure 7: Effects of micro-physics on Θ .

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