Capillary surfaces and complex analysis: new opportunities to study menisci singularities

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Outline

• Intro to wetting and capillarity

• Wetting of shaped fibers. Formulation through matched asymptotic expansion

• Hodograph method and singular menisci
Contact angle $\gamma$ and wetting phenomena

Droplet forms a finite contact angle when it meets the substrate. This angle depends on surface tensions $\sigma$, $\sigma_{sl}$ and $\sigma_{sg}$.

Hydrophobic

Hydrophilic

Flat substrate

Cylindrical fibers
Laplace’s law of capillarity.

Pressure inside the bubble $P$
Pressure outside the bubble $P^+$
Surface tension $\sigma$

Spherical drop, $R_1=R_2=R$; Hence

$$\Delta P = P - P^+ = \sigma \left( \frac{1}{R_1} + \frac{1}{R_2} \right) = \frac{2\sigma}{R}$$

Liquid cylinder:

$$\Delta P = P - P^+ = \sigma \left( \frac{1}{R_1} + \frac{1}{R_2} \right) = \frac{\sigma}{R_2}$$

W.Wick, A drop of water, Scholastic Press, NY, 1997
Laplace’s law of capillarity and minimal surfaces

Air inside and outside,

⇒

no pressure difference

\[ \Delta P = P - P^+ = 0 \]

⇒

\[ \sigma \left( \frac{1}{R_1} + \frac{1}{R_2} \right) = 0 \]

Praha’s minimal surface
Capillary rise: meniscus at the flat plate

\[ \rho \text{ – density, } g \text{ – gravity} \]

\[ \gamma \]

Force balance at the plate in \( x \)-direction

\[ -L \rho g h^2 / 2 - \sigma \sin \gamma L + \sigma L = 0 \]

\[ h = [2 \sigma (1 - \sin \gamma) / (\rho g)]^{1/2} \]

Water, \( \gamma = 0 \):
\[ h = (2 \cdot \sigma / \rho g)^{1/2} \sim 4 \text{ mm} \]

Meniscus height depends only on the materials properties of the plate/liquid pair!
Meniscus on a fiber or can a fish recognize the fiber?

Two characteristic length scales: \( R, \lambda = (\sigma / \rho g)^{1/2} \)

The Bond number: \( \varepsilon = (R / \lambda)^2 \), \( \varepsilon << 1 \) for micrometer thick fibers

\[
h_C \approx -R \cos \gamma \left[ \ln (1 + \sin \gamma) + \ln \left( e^E \sqrt{\varepsilon / 4} \right) \right]
\]

\( E = 0.57721 \)


The thinner the fiber the smaller the meniscus!

Significant difference with the plate!
Complexity of shapes of natural and man-made fibers

Spiral and grooved fibers.

Courtesy of A.Lobovsky, Advanced Fiber Engineering, NJ

Fibers from carbon nanotubes

Yarns from nanofibers produced by electrostatic spinning
Wetting of shaped fibers
Mechanism of wetting of elliptical fibers

\[ L_{\text{min}} \] (minimum elevation)

\[ L_{\text{max}} \] (maximum elevation)

Round cross-section

Elliptical cross-section

Air

Liquid

\[ L_{\text{r}} \]

\[ L_{\text{el}} \]

Air

Liquid
Radii of curvature of sags and bulges on contact line

Capillary pressure pushes meniscus from the sharp edges toward the wider part where the curvature is smaller.

\[ R_c \] – radius of curvature of the sag

A. Trofimov, and V. Vekselman,
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Capillary rise. Laplace equation in Cartesian coordinates

Profile of the free surface

\[ Z = H(X,Y) \]

Normal vector to the free liquid surface

\[ \mathbf{N} = \left(1 + | \nabla H |^2 \right)^{-1/2} \begin{pmatrix} -\frac{\partial H}{\partial X} \\ -\frac{\partial H}{\partial Y} \\ 1 \end{pmatrix} \]

Laplace equation of capillarity with the body force = gravity

\[ -\sigma \nabla \cdot \mathbf{N} - \rho g H = 0 \]

\[ \sigma \nabla \cdot \left[ \left(1 + | \nabla H |^2 \right)^{-1/2} \nabla H \right] - \rho g H = 0 \]
Boundary conditions

\( \Gamma \) is the fiber profile in the \((X,Y)\) - section

Introducing the unit normal vector \( \mathbf{n} = (n_x, n_y, 0) \) pointing to the fiber exterior, the Young equation reads

\[
\Gamma : \quad \mathbf{N} \cdot \mathbf{n} = \cos \gamma.
\]

\[
(1 + |\nabla H|^2)^{-1/2} \left( \frac{\partial H}{\partial X} n_x + \frac{\partial H}{\partial Y} n_y \right) = -\cos \gamma.
\]

At infinity where the meniscus levels off, we have

\[
r = \sqrt{X^2 + Y^2} \to \infty : \quad H \to 0
\]
Math model in dimensionless variables

\[ r(x, y) = \frac{R}{L_{\text{fiber}}}, \quad L_{\text{fiber}} = \sqrt{\text{area}} \]

\[ h = \frac{H}{\sqrt{\sigma / \rho g}} \]

\[ \Omega: \quad \nabla \cdot \left[ \left( 1 + |\nabla h|^2 \right)^{-1/2} \nabla h \right] - \varepsilon \cdot h = 0 \]

\[ \Gamma: \quad \left( 1 + |\nabla h|^2 \right)^{-1/2} \frac{\partial h}{\partial n} = -\cos \gamma \]

\[ r = \sqrt{x^2 + y^2} \to \infty: \quad h \to 0 \]

**Numerics:**


Surface evolver by K.Brakke, [http://www.susqu.edu/brakke/evolver/evolver.html](http://www.susqu.edu/brakke/evolver/evolver.html)
Method of matched asymptotic expansions, $\varepsilon << 1$


**Working hypothesis:**

Two regions, two different asymptotics: In the inner region, the shape of meniscus is significantly affected by the fiber shape.

$x, y \sim O(1)$:

\[ h^i(x, y) = h^{i,0}(x, y) + O(\varepsilon), \]

\[ \Omega : \nabla \left[ \left( 1 + |\nabla h^{i,0}|^2 \right)^{-1/2} \nabla h^{i,0} \right] = 0 \]

In the outer region, $x, y \sim O(1/\sqrt{\varepsilon})$, the shape of meniscus is universal and is described by a linear equation

\[ \Delta h - \varepsilon \cdot h = 0 \]

\[ r = \sqrt{x^2 + y^2} \rightarrow \infty : \quad h \rightarrow 0 \]
Outer region,

\[ x, y \sim O(1/\sqrt{\varepsilon}) \]

\[ \Delta h - \varepsilon \cdot h = 0 \]

\[ r = \sqrt{x^2 + y^2} \to \infty : \quad h \to 0 \]

General solution:

\[ h^{o,0}(r, \varphi) = C_0 K_0(r\sqrt{\varepsilon}) + \sum_{n=1}^{\infty} K_n(r\sqrt{\varepsilon}) \left[ C_n \cos(n\varphi) + D_n \sin(n\varphi) \right] \]

\[ K_n(r\sqrt{\varepsilon}) \quad \text{are the modified Bessel functions, constants } C_n \text{ ???} \]

Observe that all ripples become circular at infinity; same phenomenon is shaping meniscus…

In the leading order, the shape of meniscus is described by the boxed term.
Linking two expansions by the first integral

Integrate over $\Omega$

$$-\nabla \cdot \mathbf{N} - \varepsilon \cdot h = 0 \Rightarrow$$

$$l \cos \gamma = \varepsilon \iint_{\Omega} h d\Omega$$

where $l$ is the dimensionless fiber perimeter.

$$\varepsilon \iint_{\Omega} h d\Omega = \varepsilon \iint_{\Omega \cap C_M} h d\Omega + \varepsilon \iint_{\Omega \setminus C_M} h d\Omega \approx \varepsilon \iint_{\Omega \cap C_M} h^i d\Omega + \varepsilon \iint_{\Omega \setminus C_M} h^0 d\Omega$$

Inner expansion of the outer expansion specifies $C_0$ and provides the boundary condition for the inner problem

$$[h^{o,0}]^i = \frac{l \cos \gamma}{2\pi} K_0 \left( r \sqrt{\varepsilon} \right) \bigg|_{r \approx 1} \approx -\frac{l \cos \gamma}{2\pi} \left[ \ln r + \ln \left( \frac{e^E \sqrt{\varepsilon}}{2} \right) \right], \quad E = 0.5772$$
Meniscus on an arbitrarily shaped fiber as a problem of minimal surfaces

\[
\begin{align*}
\Omega: & \quad \nabla \cdot \left[ \left( 1 + |\nabla h|^2 \right)^{-1/2} \nabla h \right] = 0 \\
\Gamma: & \quad \left( 1 + |\nabla h|^2 \right)^{-1/2} \frac{\partial h}{\partial n} = -\cos \gamma \\
r \to \infty: & \quad h(r, \varphi) \approx -\frac{l \cos \gamma}{2\pi} \left[ \ln r + \ln \left( \frac{e^E \sqrt{\varepsilon}}{2} \right) \right]
\end{align*}
\]

When \( h \) is obtained, meniscus shape is calculated using the van Dyke construction:

\[
h^{\text{meniscus}}(x, y) = h(x, y) + \frac{l \cos \gamma}{2\pi} \left[ K_0 \left( r\sqrt{\varepsilon} \right) + \ln r + \ln \left( \frac{e^E \sqrt{\varepsilon}}{2} \right) \right]
\]
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**Analogy: 2D flow of non–Newtonian fluids through porous media**


<table>
<thead>
<tr>
<th>$\Omega$:</th>
<th>$\nabla \cdot \mathbf{J} = 0, \quad \nabla h = -\Phi(J) \mathbf{J}/J$</th>
</tr>
</thead>
</table>

**Continuity equation** | **Non-linear Darcy’s equation with flux $J$**

$$|\nabla h| = \Phi(J), \quad \Phi(J) = \frac{J}{\sqrt{1 - J^2}},$$

$\Phi(J) \geq 0, \quad \Phi'(J) \geq 0$

<table>
<thead>
<tr>
<th>$\Gamma$:</th>
<th>$\mathbf{J} \cdot \mathbf{n} = \cos \gamma$</th>
<th>At the fiber surface the normal component of the flux is constant</th>
</tr>
</thead>
</table>

$$r \to \infty: h(r, \varphi) \approx -\frac{l \cos \gamma}{2\pi} \left[ \ln r + \ln \left( \frac{e^E \sqrt{\varepsilon}}{2} \right) \right]$$
The stream function

\[ \nabla \cdot \mathbf{J} = 0, \quad \Rightarrow \quad J_x = \frac{\partial \psi}{\partial y}, \quad J_y = -\frac{\partial \psi}{\partial x} \]

Two equivalent pairs

\[ J = |\mathbf{J}| > 0, \quad J_x = J \cos \theta, \quad J_y = J \sin \theta \]

Assumption on the functional behavior

\[ \psi(J, \theta) \quad \quad h(J, \theta) \]
Hodograph transformation for the stream function $\psi(J, \theta)$ and meniscus height $h(J, \theta)$

\[
J \left(1 - J^2\right)^{1/2} \frac{\partial \psi}{\partial J} = -\frac{\partial h}{\partial \theta}, \quad \frac{\partial \psi}{\partial \theta} = J \left(1 - J^2\right)^{1/2} \frac{\partial h}{\partial J}
\]

Sokolovsky transformation

\[
t = \ln \left(1 + \sqrt{1 - J^2}\right) - \ln J \equiv \text{arccosh} \left(J^{-1}\right)
\]

Leading to the Cauchy–Riemann equations

\[
\frac{\partial \psi}{\partial t} = \frac{\partial h}{\partial \theta}, \quad \frac{\partial \psi}{\partial \theta} = -\frac{\partial h}{\partial t}
\]

And complex potentials

\[
W = -h + i\psi, \quad \chi = t + i\theta
\]

Chaplygin relations with the (x,y) coordinates

\[
dx = -\cos \theta \sinh t \, dh - \sin \theta \cosh t \, d\psi, \\
\]

\[
dy = -\sin \theta \sinh t \, dh + \cos \theta \cosh t \, d\psi.
\]
Example: meniscus on a circular cylinder

Using the \((\theta,t)\) plane, one infers:

\[
\frac{\partial^2 h}{\partial t^2} = 0 \quad \text{implying}
\]

\[
h = C_1 t + C_2
\]

With the aim of the boundary conditions one, reproduces Lo’s solution

\[
h = -\cos \gamma \left[ \ln \left( r + \sqrt{r^2 - \cos \gamma^2} \right) + \ln \left( e^E \sqrt{\varepsilon} / 4 \right) \right]
\]
Meniscus on a oval fiber with $\gamma = 0$

Hodograph plane  
Plane of complex potential

Using `inverse' method of truncated Fourier series:

$$W(\chi) = -h_o + \frac{l}{2\pi} \chi + a(e^{-2\chi} - 1)$$

And follow the grid

$$\Gamma_j : \chi = t_j + i\theta, \quad \text{where} \quad \theta \in [0, \pi]$$
Singularities of contact line on smooth fibers

Singularities of contact line on fibers with sharp edges

When the model of a locally flat liquid surface becomes incompatible with the contact angle condition?

Cross-section

Shaded region corresponds to the solid fiber
Shaping menisci at the chemically uniform edges

Laplace equation in cylindrical coordinates

\[ \sigma \left[ \frac{1}{r} \frac{\partial}{\partial r} \left( Gr \frac{\partial H}{\partial r} \right) + \frac{1}{r} \frac{\partial}{\partial \varphi} \left( \frac{G \partial H}{r \partial \varphi} \right) \right] \approx 0 \]

Gravity is less important

\[ G(r, \varphi) = \left[ 1 + \left( \frac{\partial H}{\partial r} \right)^2 + \frac{1}{r^2} \left( \frac{\partial H}{\partial \varphi} \right)^2 \right]^{-1/2} \]

Similarity solution

\[ H(r, \varphi) = rF(\varphi) + \text{const} \]

Solution

\[ (F + F'')(1 + F^2) \left( 1 + F^2 + F'^2 \right)^{3/2} = 0 \]

\[ F(\varphi) = A_1 \cos \varphi + A_2 \sin \varphi \]
Domains of analyticity

\[ \sin^2 \varphi_{\Gamma} - \cos^2 \gamma = -\cos(\gamma + \varphi_{\Gamma}) \cos(\gamma - \varphi_{\Gamma}) > 0 \]

Generalization of the Concus-Finn condition

Square of admissible angles where continuous solution exists.


P. Concus and R. Finn, PNAS, 63 (2), 292 (1969)
Illustration of the meniscus shape at the edge of a polypropylene film that has been dipped in a syrup. The arrows on the magnified image indicate a jump of the end point of the contact line along the film edge.
Conclusions

• Profile of menisci on the complex shaped fibers is mostly controlled by capillary and wetting forces: effect of meniscus weight is insignificant for microfibers.

• On elliptical fibers having two different curvatures, the contact line sags down and bulges up. The height difference between these two limiting points can be significant.

• Mathematical model of meniscus on a slender fiber is reduced to a model of a minimal surface supported by a fiber of the given shape.

• Contact line may have singularities even on smooth fibers!

• Domain of analyticity of the contact meniscus meeting the V–type edges is specified for chemically homogeneous and heterogeneous sides and V–angles. New type of singularity with a finite jump on the contact line was discovered.