Experimental and Theoretical Study
of Motion of Drops on
Horizontal Solid Surfaces with a
Wettability Gradient

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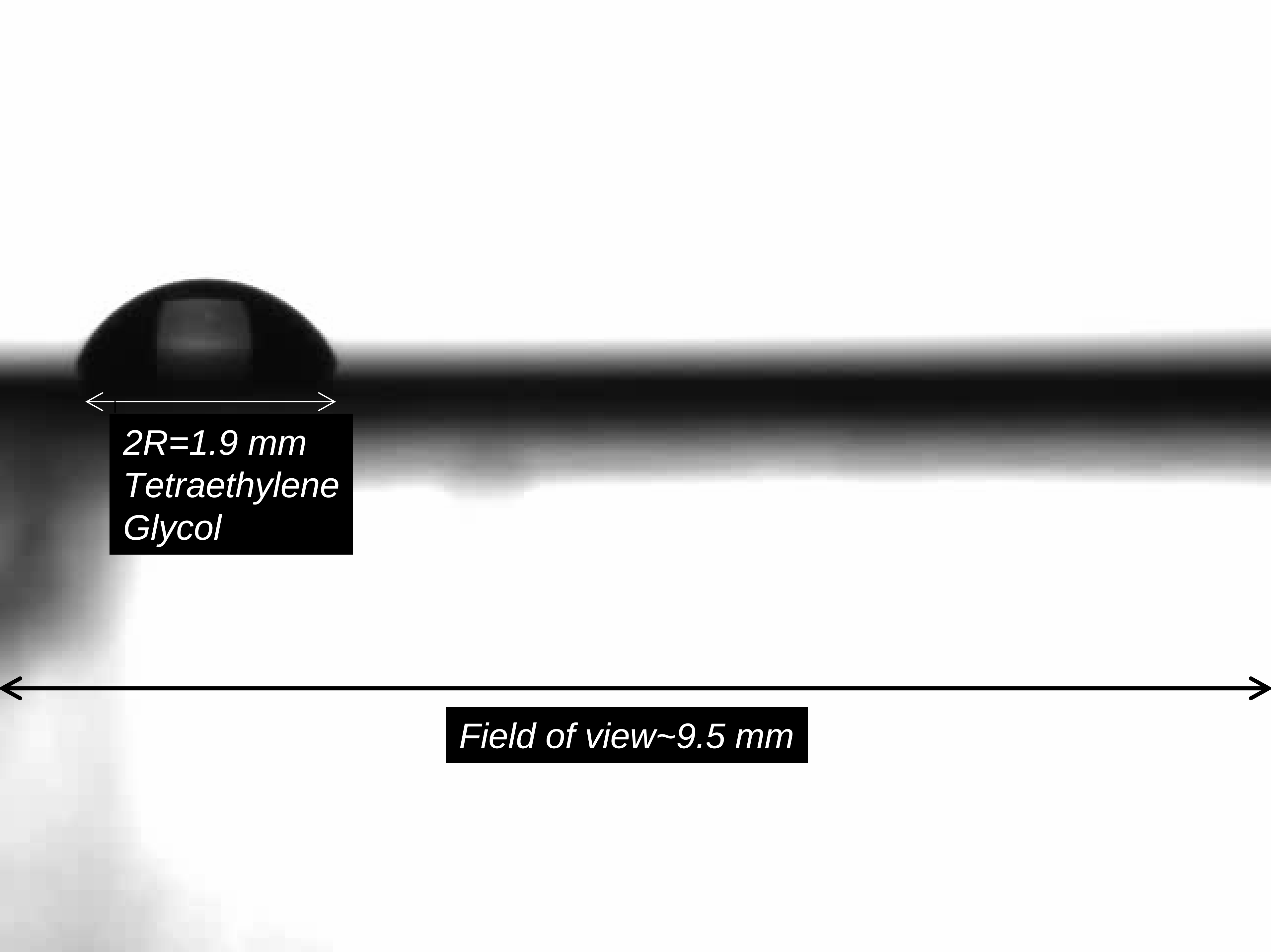
Outline

- Background
- Motivation
- Literature review
- Objectives
- Experimental work and results
- Theoretical work
- Theory vs. experiments
- Conclusion

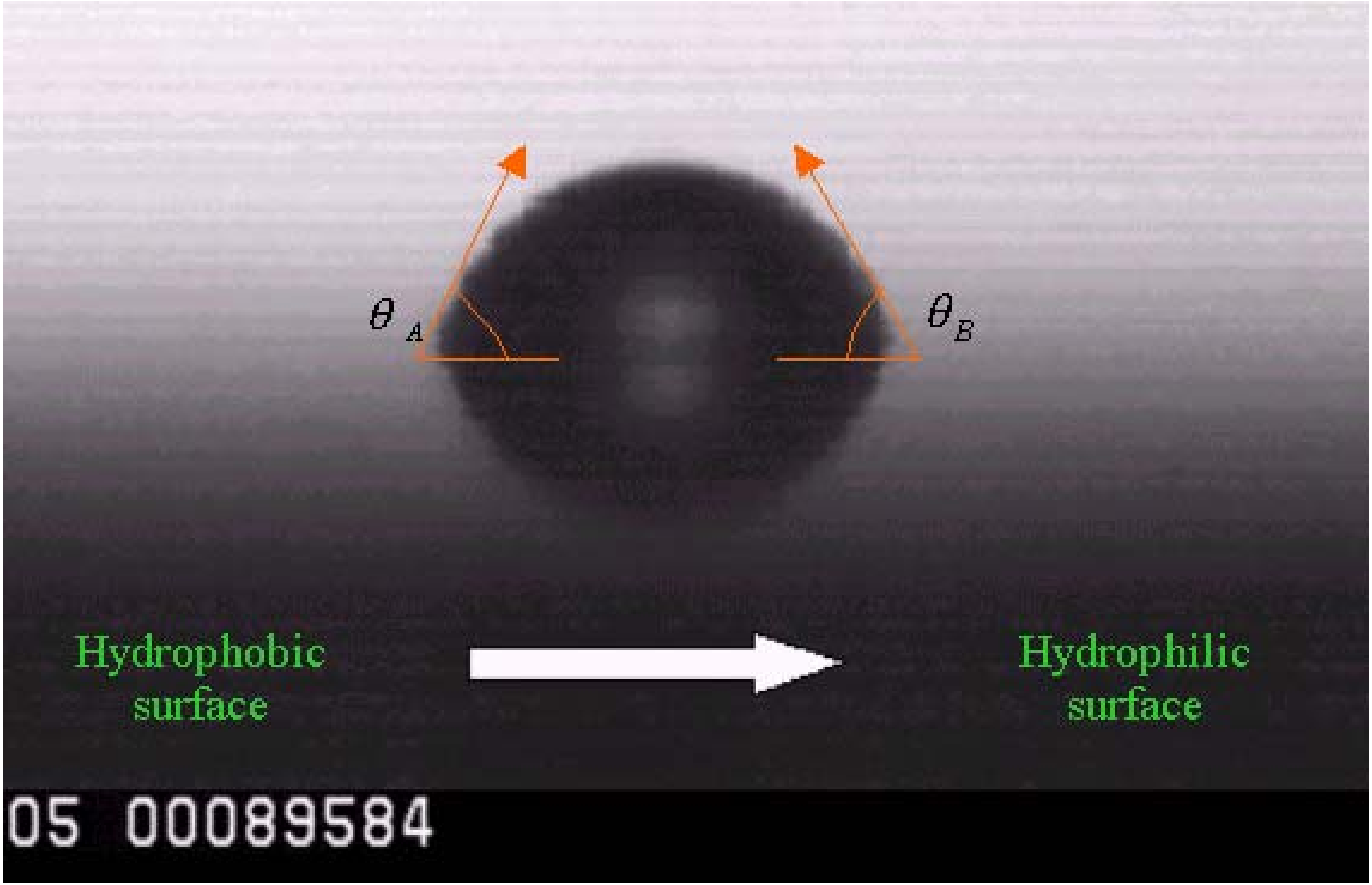
Background

- We observe the phenomenon of drop motion almost every day.
- When a liquid drop is introduced on a horizontal surface, it may spread radially if it wets the surface, but its center of mass does not move.

  - Thermocapillarity (Marangoni effect)
  - Wettability gradient (gradient of surface energy)


2R=1.9 mm
Tetraethylene
Glycol
Field of view~9.5 mm

What makes the drop move?



Motivation

- This motion can be useful in

  - Moving drops in “laboratory-on-a-chip” type MEMS applications.

  - Debris removal in ink jet printing

  - Condensation heat transfer

Literature Review

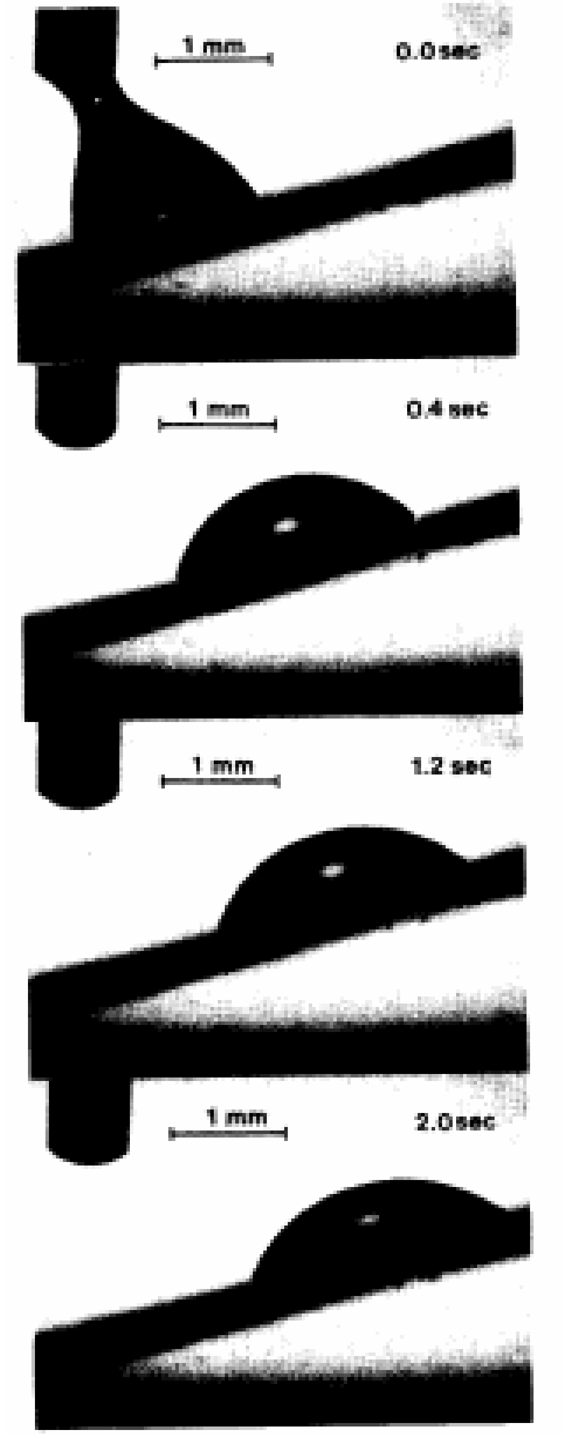
Theory

- Greenspan (1978) inspired by the work of Carter (1967) stated that drops would migrate on surfaces with a wettability gradient.

- Brochard (1989)
  - Assumed a weak gradient with a small contact angle
  - Used the “unbalanced Young force” to estimate the driving force.

- Ford and Nadim (1994)
  - Motion driven by temperature gradient
  - The droplet was modeled as an infinitely wide strip with a finite length and an arbitrary height (2-D)

Experiments



- Chaudhury and Whitesides (1992) prepared wettability gradient by modifying the method of Elwing et al. (1987).

- Water drops of volume 1 to 2 μl, moved at 1-2 mm/s).

Experiments

- Daniel el al. (2001) observed more rapid motion (1.5 m/s) of similar water drops when condensation occurred on cold surfaces.

- Daniel and Chaudhury (2002) investigated the motion of ethylene glycol drops on surfaces with a wettability gradient.

- Daniel et al. (2004) performed experiments using a variety of liquids, reporting results for velocities that were enhanced considerably when the substrate was vibrated.

Conclusion of the literature review

- The few theoretical models have all employed the lubrication approximation.
- None of the models is able to predict the observed velocities.
- Daniel et al.(2001, 2002, 2004) did not compare predictions from any theory with velocities they measured.
- Daniel et al. reported a single velocity for each drop size. The velocity should depend on position in a wettability gradient.
- There is a need for a systematic study aimed at understanding this phenomenon. Both theory and experiments are needed.

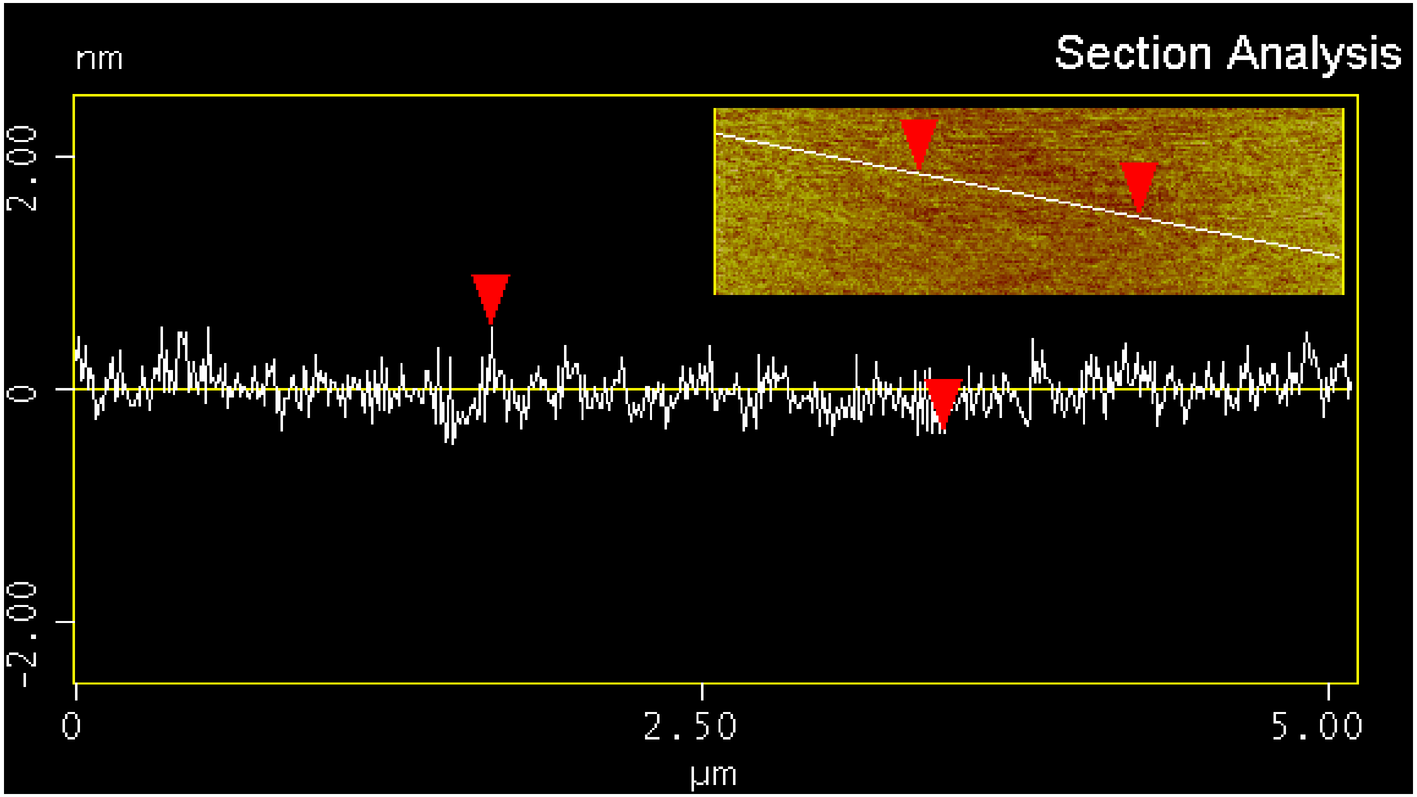
Objectives

- To develop a theoretical understanding and description of this phenomenon.
- To measure the migration velocities of drops of a range of sizes.
- To measure the contact angle on the wettability gradient surface.
- To empirically establish the scaling laws governing this phenomenon.
- To compare the measured velocities with predictions from theory.

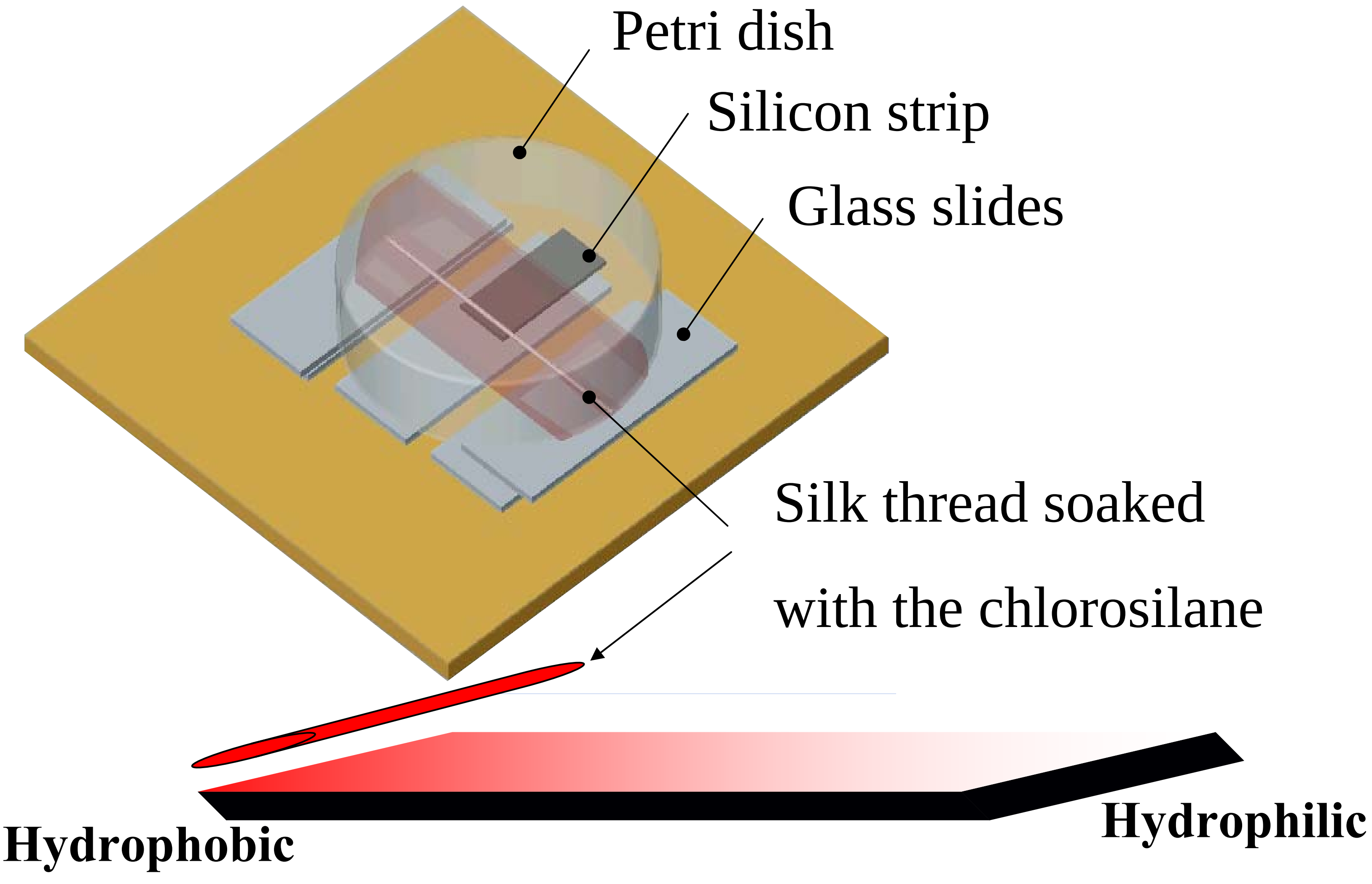
Experimental Work and Results

Surface quality analysis

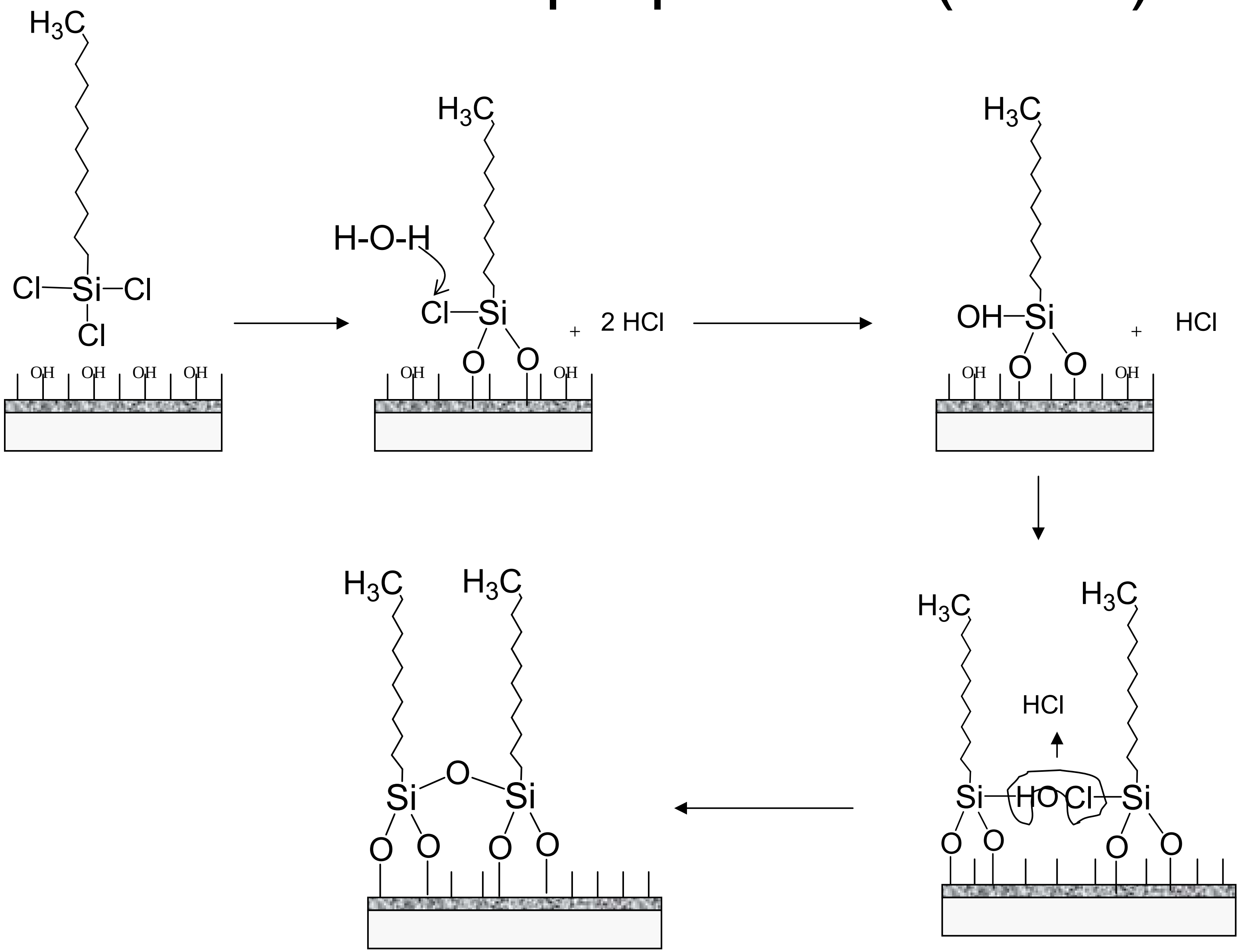
- Silicon wafer (4/P/100/B, **prime grade**)
- RMS < 0.2 nm
- Max. height = 0.9 nm



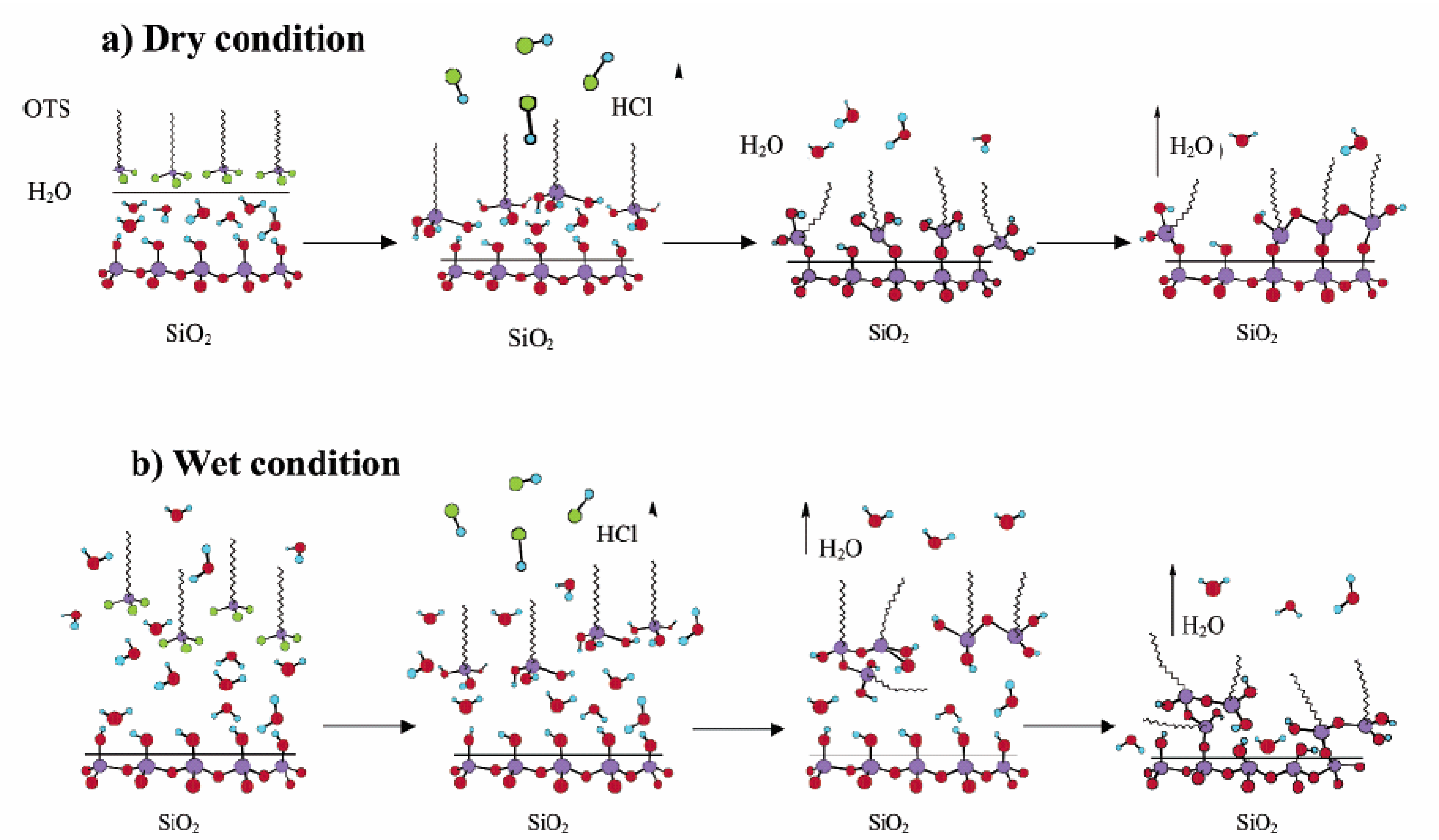
Wettability gradient preparation



Gradient preparation (Cont.)

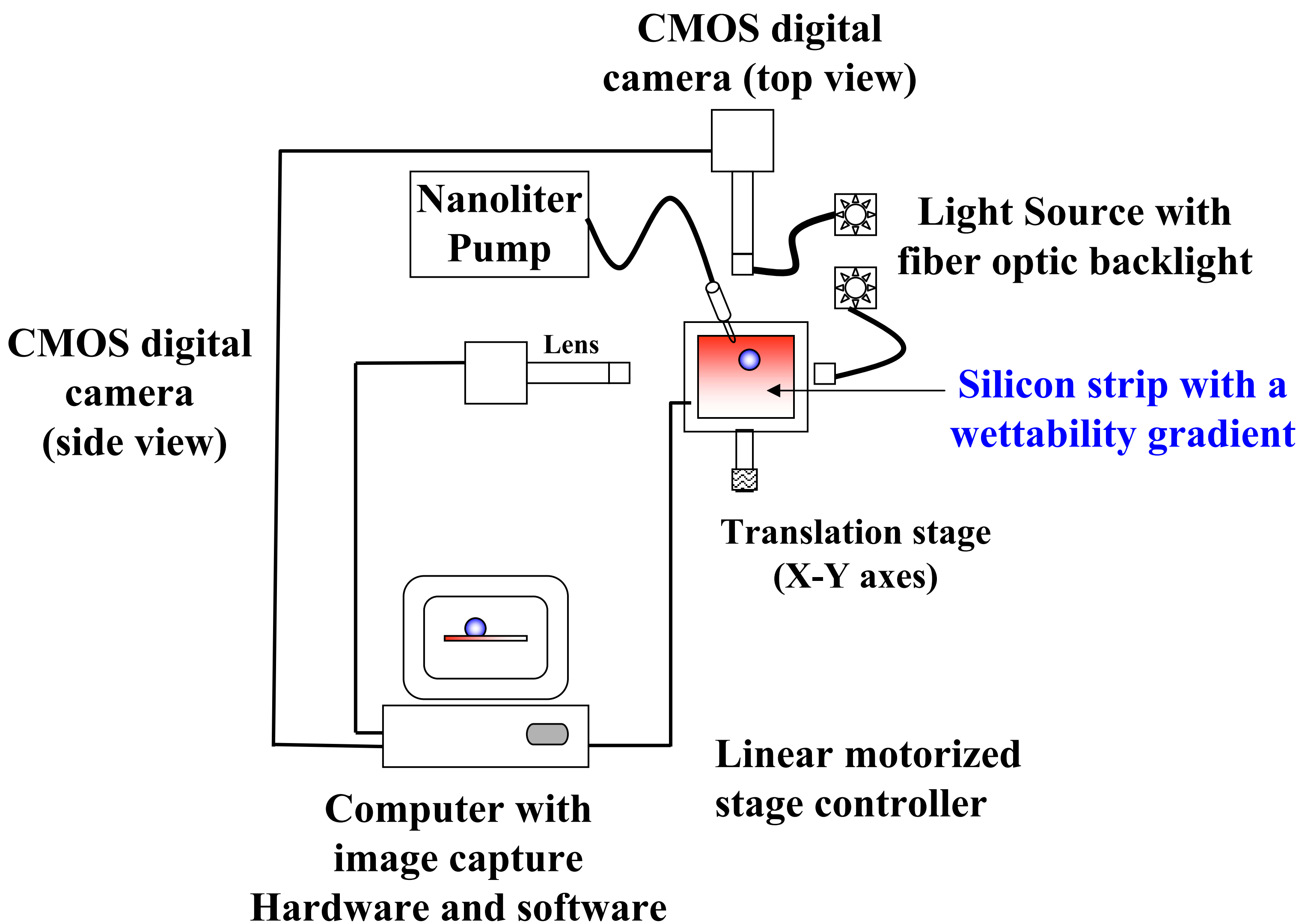


Proposed reaction mechanisms



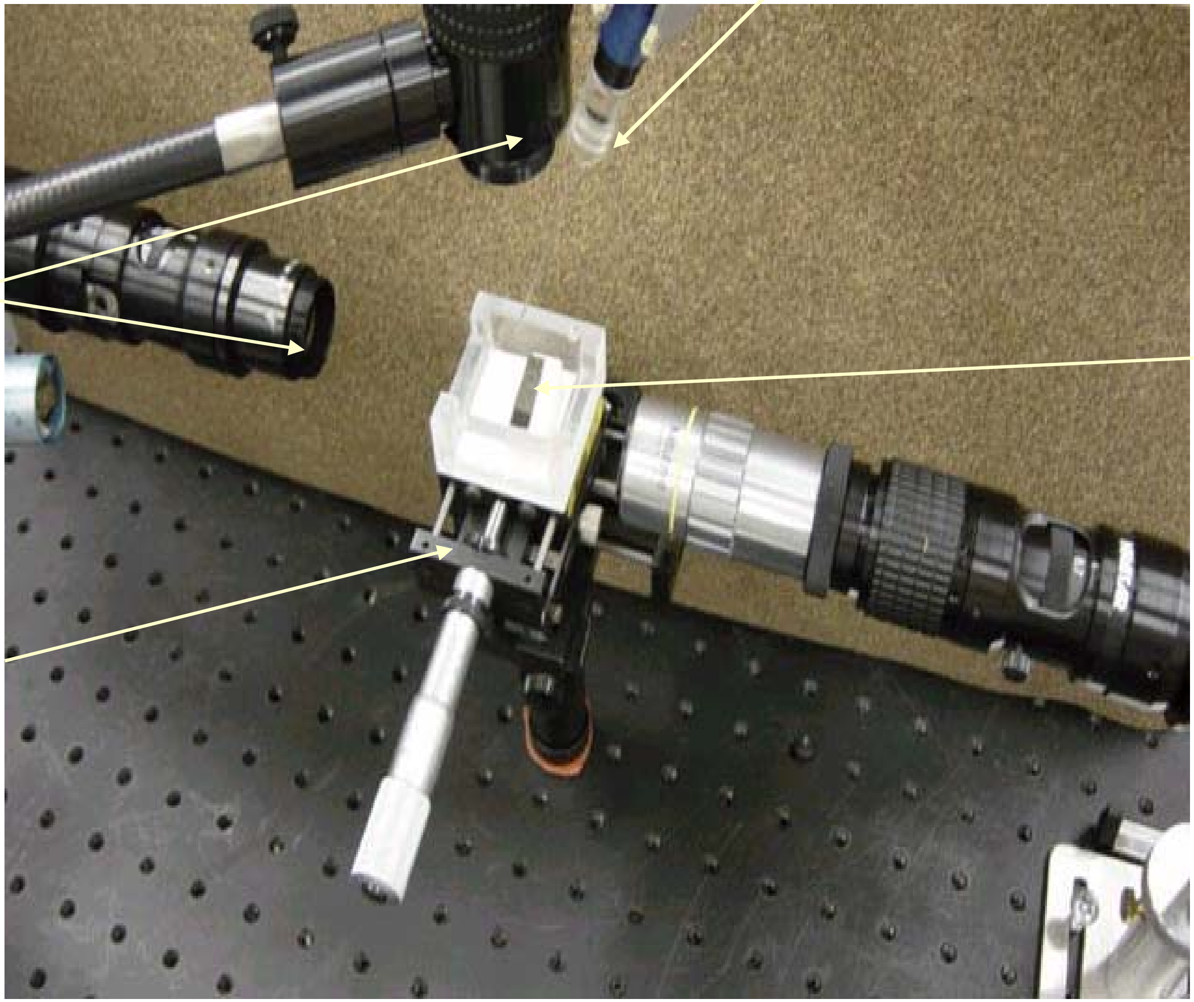
Yuliang Wang and Marya Lieberman, *Langmuir, Vol. 19, No. 4, 2003*

Schematic of the experimental apparatus



Experimental apparatus

Liquid introduced via a Nanoliter pump tip

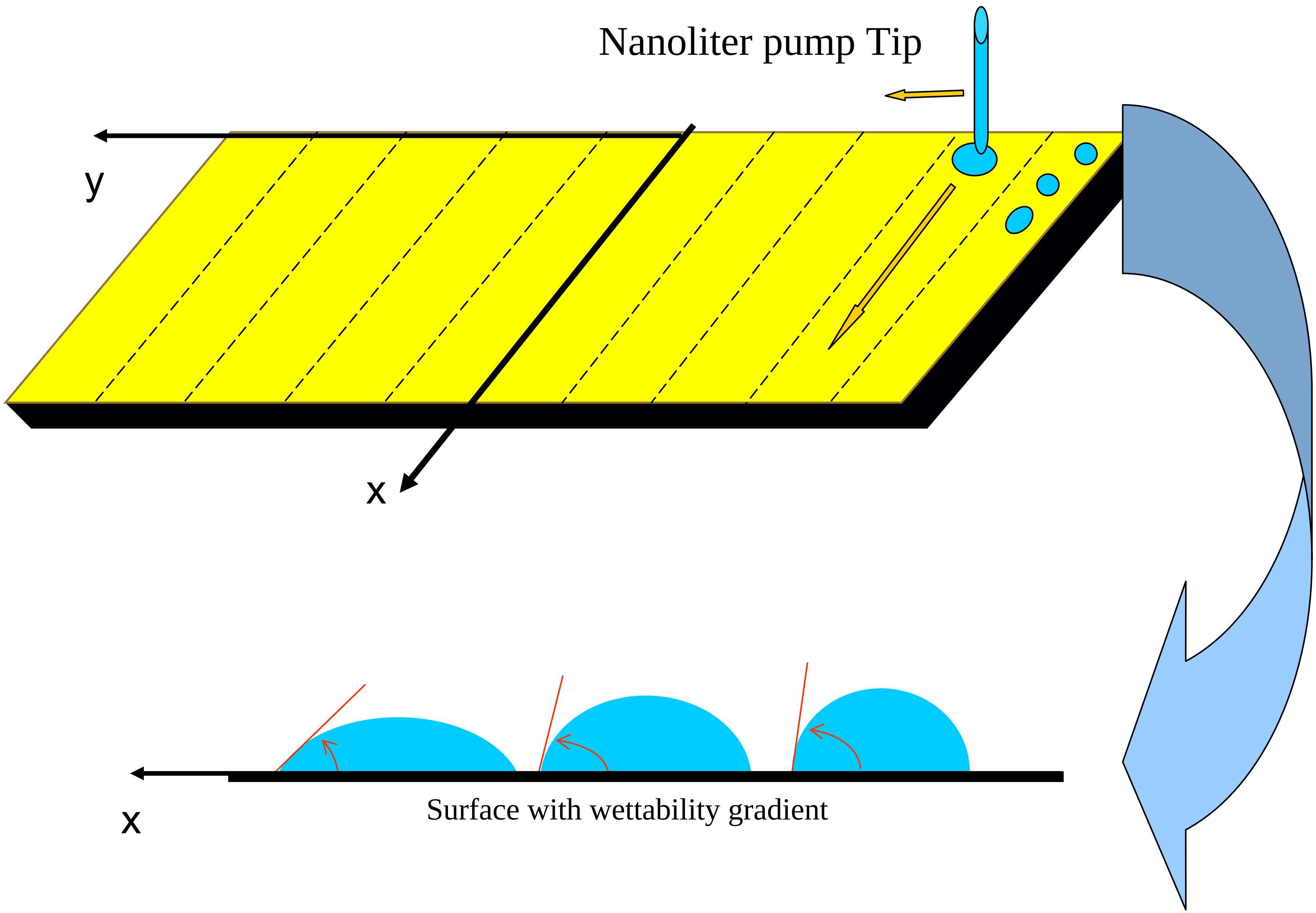


Camera lenses

Silicon strip with **wettability gradient**

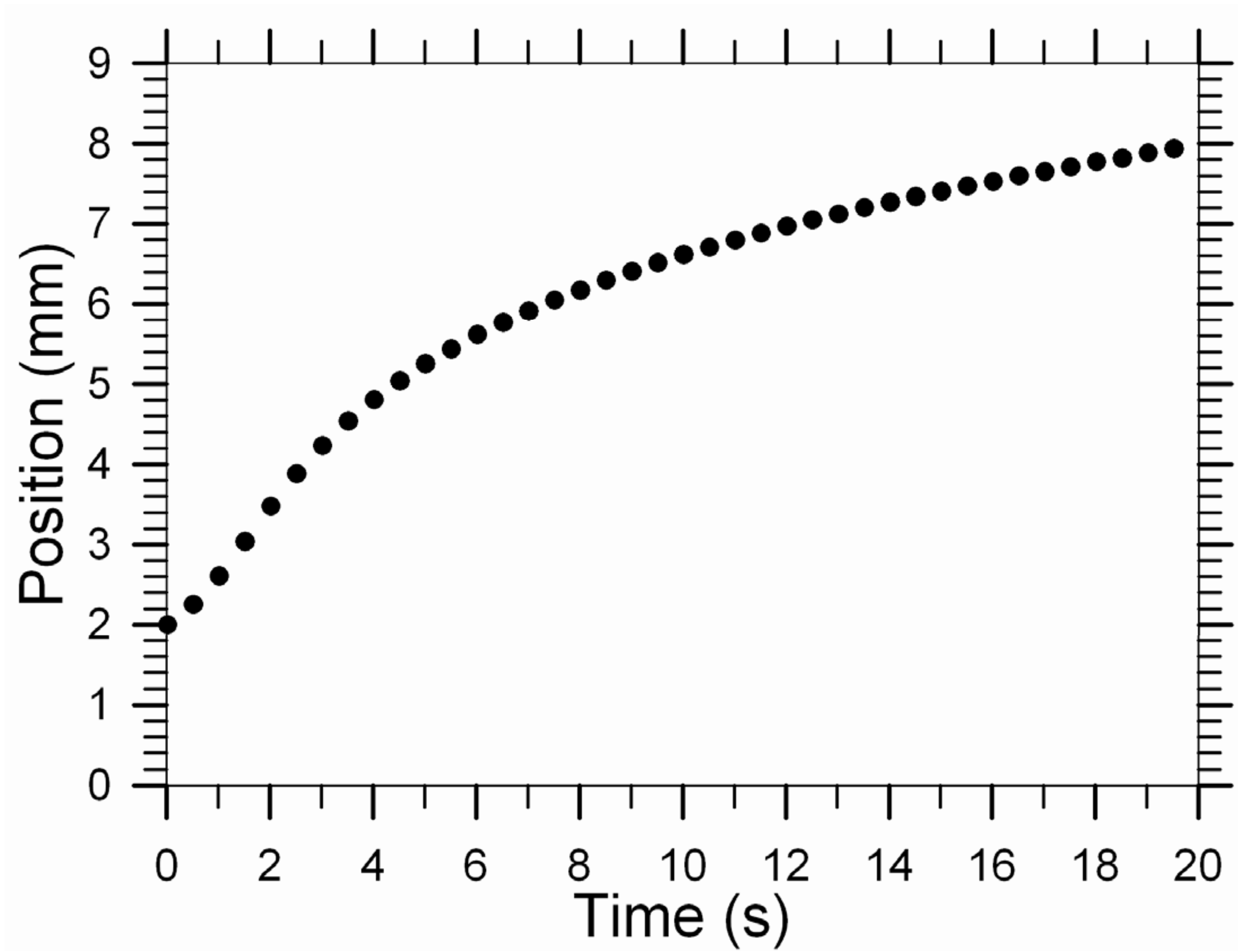
Micrometer translation stage

Experiment procedure

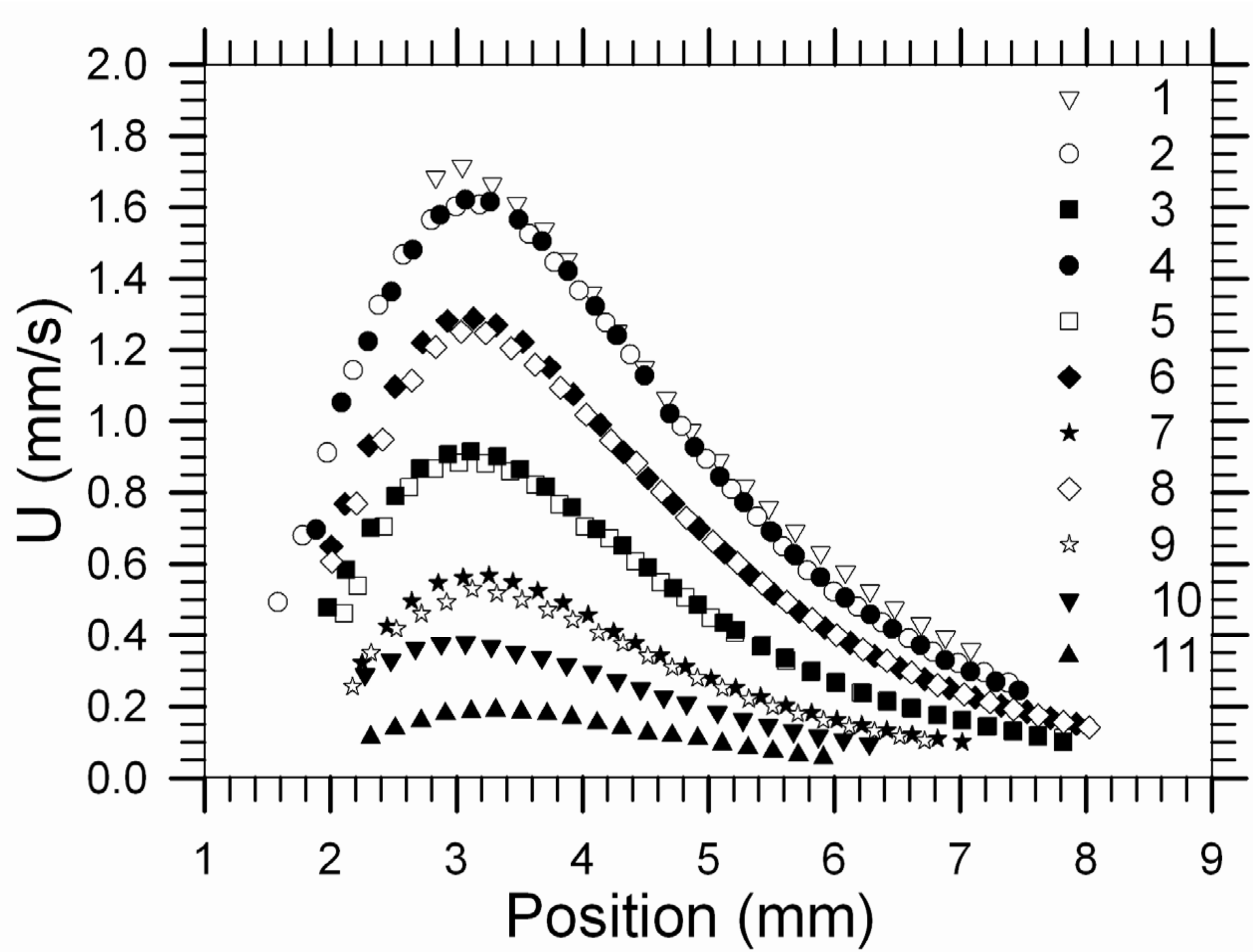


Velocity measurement procedure

Position versus Time

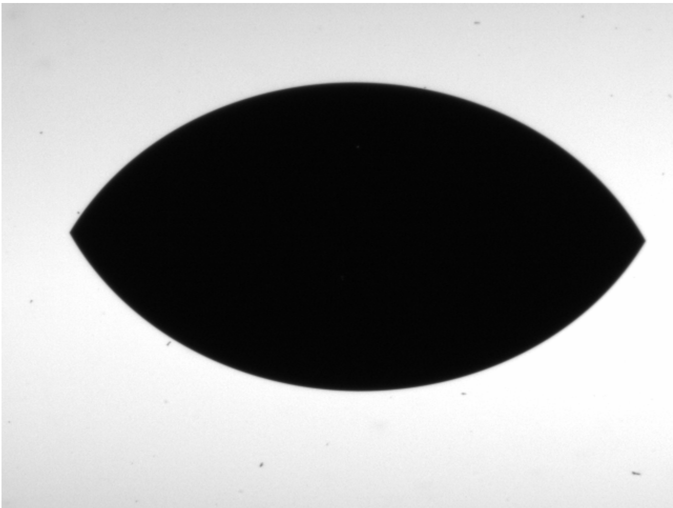


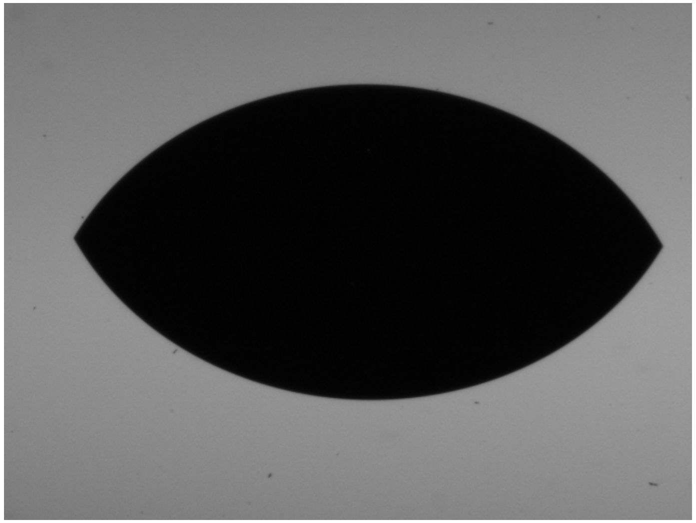
Instantaneous velocity

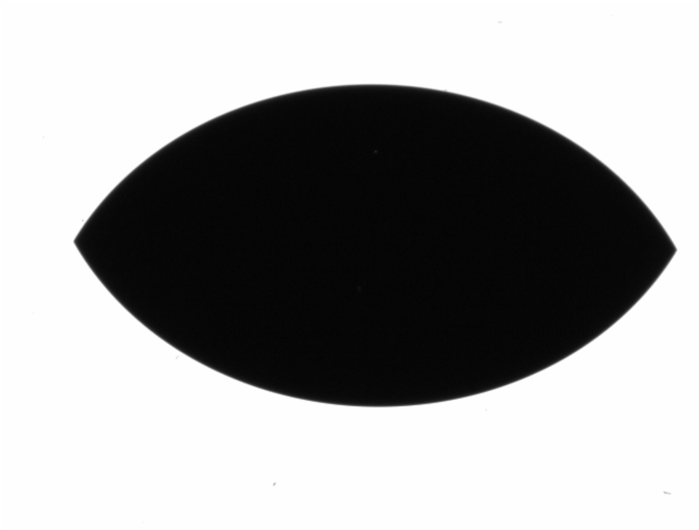


Contact angle measurement procedure

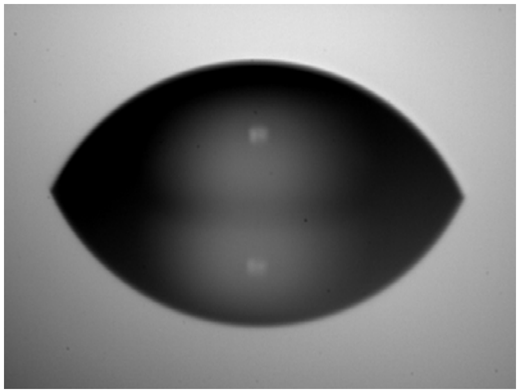
Image quality (Lighting conditions)



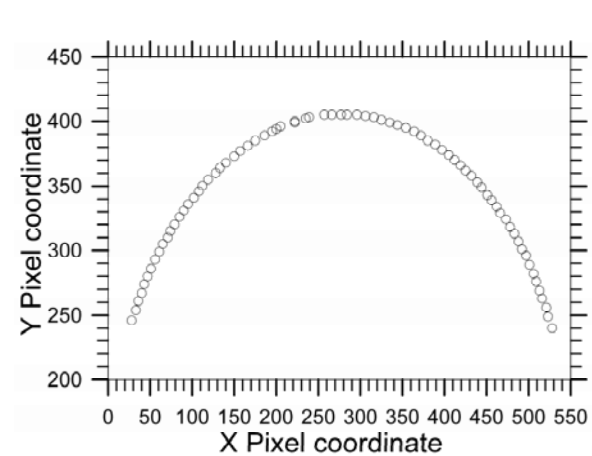




Procedure



Canny edge detector
To find the **drop profile**

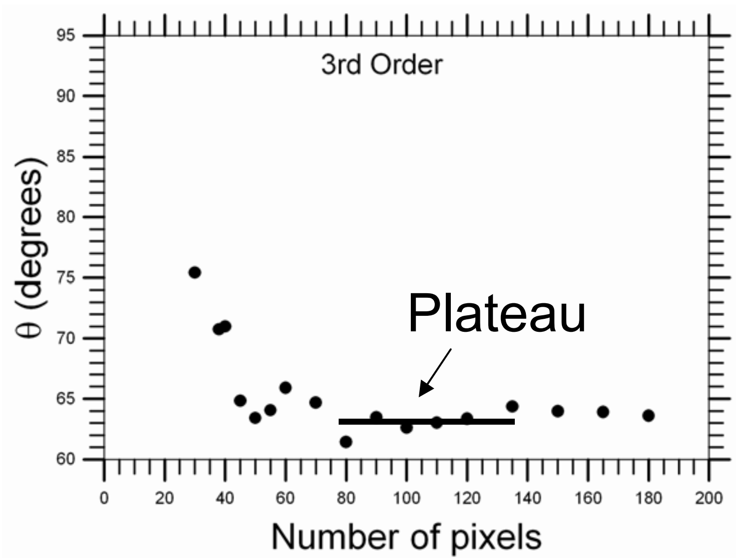


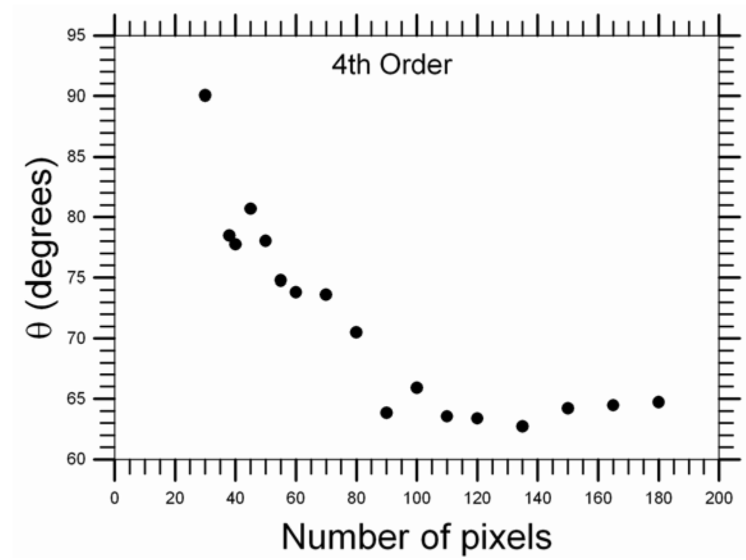
10~20 μm of the interface is unusable due to distortion

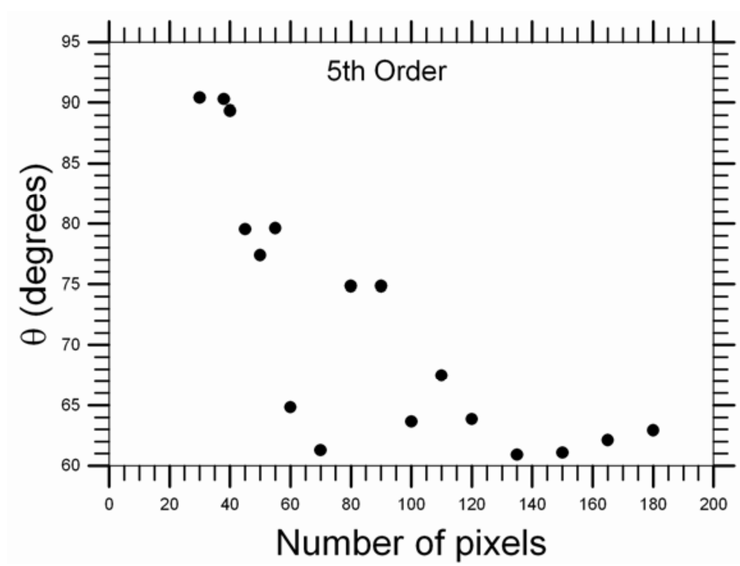
Perform a polynomial fit

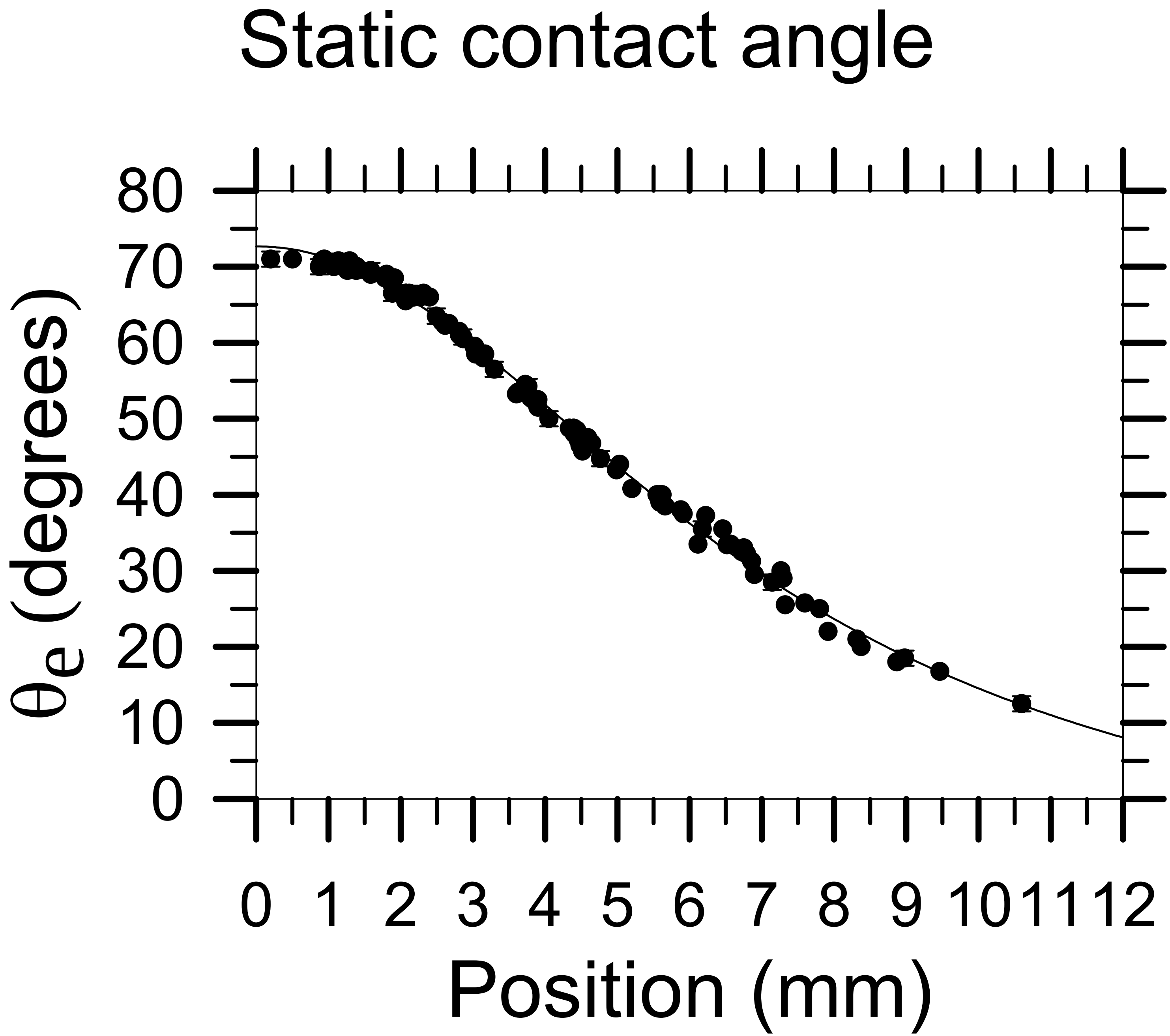
Extrapolate the fit to the surface, and the slope is $\tan(\theta)$

Fitting

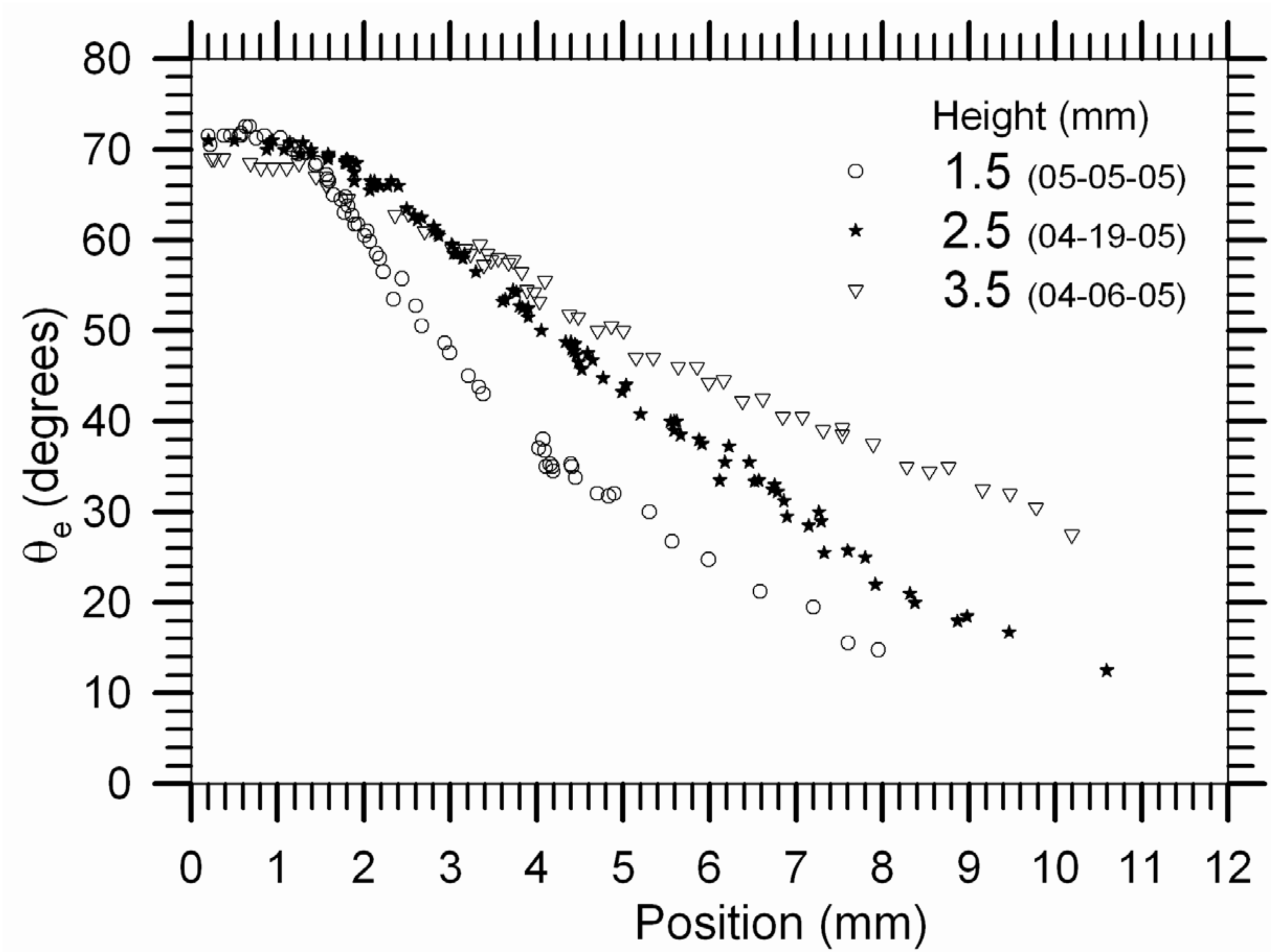

3rd Order
Plateau
θ (degrees)
95
90
85
80
75
70
65
60
0 20 40 60 80 100 120 140 160 180 200
Number of pixels


4th Order
θ (degrees)
95
90
85
80
75
70
65
60
0 20 40 60 80 100 120 140 160 180 200
Number of pixels


5th Order
θ (degrees)
95
90
85
80
75
70
65
60
0 20 40 60 80 100 120 140 160 180 200
Number of pixels


Static contact angle
80
70
60
50
40
30
20
10
0
θe (degrees)
0
1
2
3
4
5
6
7
8
9
10
11
12
Position (mm)

Variable steepness in wettability gradient



Theoretical Work

Langmuir **2005,** *21,* 11844−11849

Motion of a Drop on a Solid Surface Due to a Wettability Gradient

R. Shankar Subramanian,* Nadjoua Moumen, and John B. McLaughlin

Langmuir **2005**

Parameters

Dimensional analysis:

- Reynolds number $\mathrm{Re} = \frac{VR}{\nu}$
- capillary number $Ca = \frac{\mu V}{\gamma}$
- Bond number $Bo = \frac{\rho g R^2}{\gamma}$

Scaled drop velocity will depend on these parameters.

Range of values of the parameters

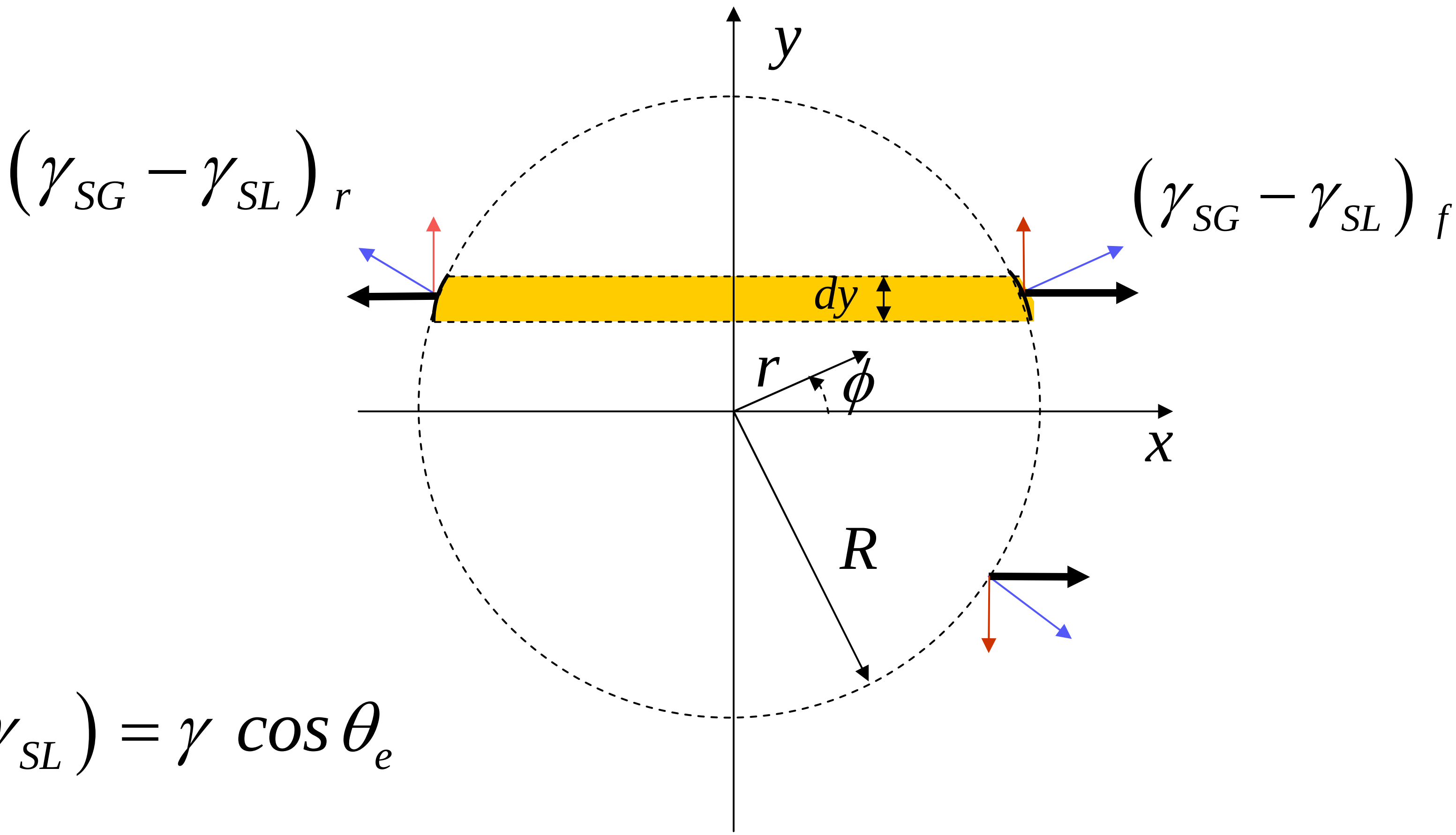
Using the measured velocity V

- **Re ~ 10^{-2} – 10^{-4} (Stokes motion)**
- **Ca ~ 10^{-3} – 10^{-5} (static shape)**
- **Bo ~ 0.7 – 0.03 (spherical cap)**

Quasi-steady approximation

- **Newton transient time scale**, in which a drop of mass *m* accelerates to its steady velocity is $0.02 - 0.2\, ms$
- **Viscous relaxation time scale**, in which the viscous drag relaxes to its steady description in a transient analysis can be estimated to be $R^2 / \nu = 4 - 64\, ms$
- The time scale, in which the drop moves a distance equal to its footprint diameter is typically $0.5\ \mathrm{s}$ in the sharpest part of the gradient

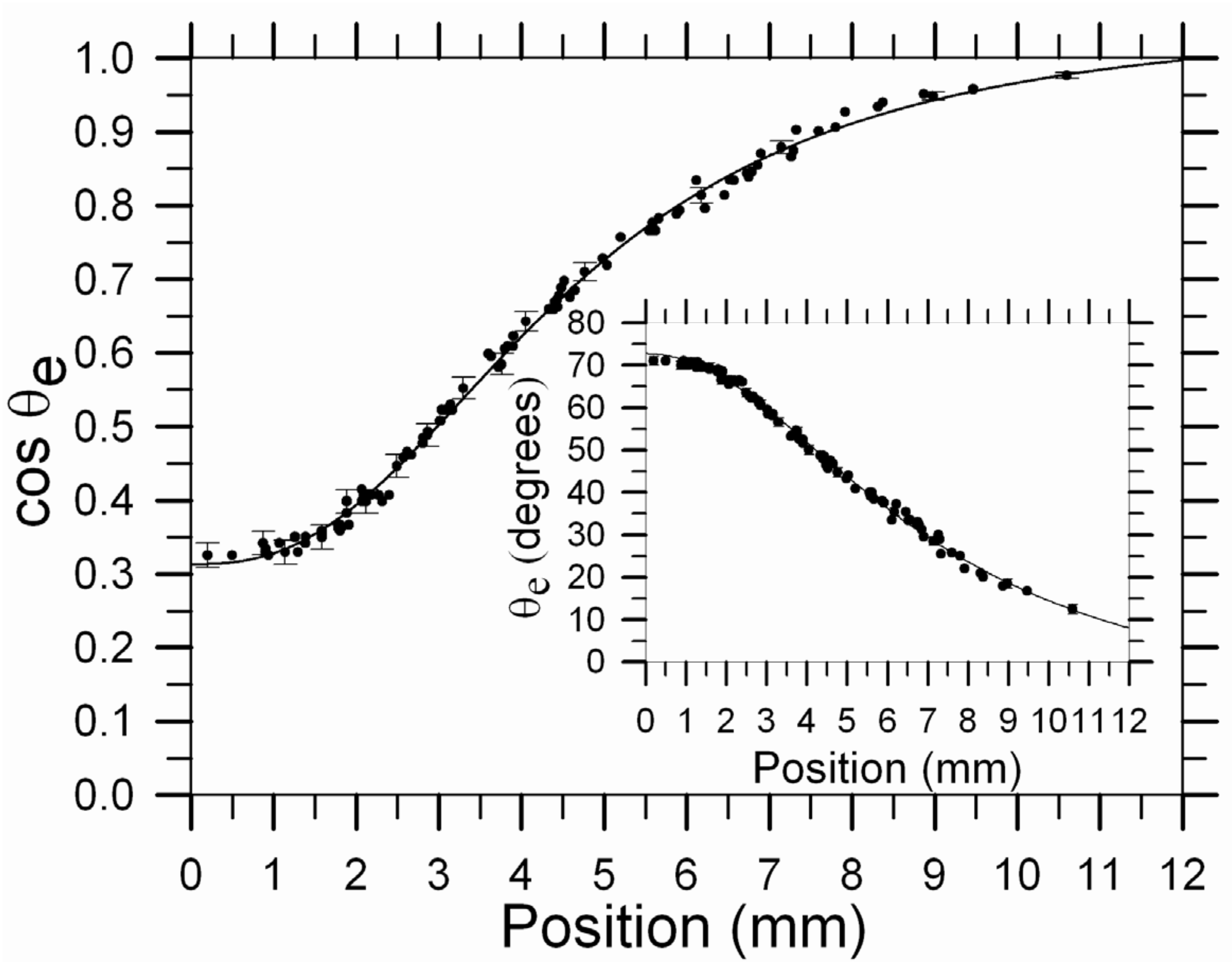
Driving force



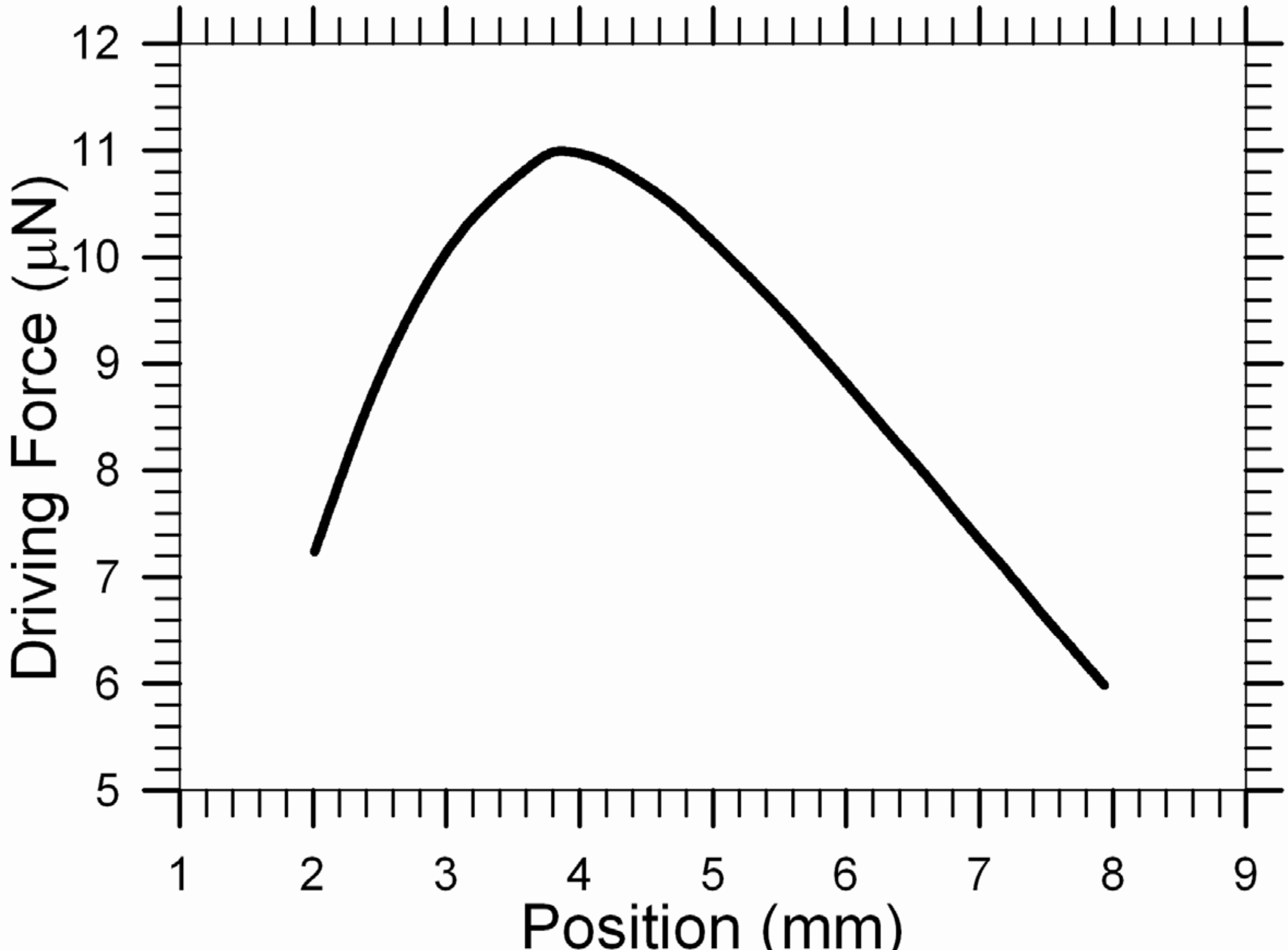
$$\left(\gamma_{SG}-\gamma_{SL}\right)=\gamma\cos\theta_e$$

$$F_{Driving}=2\gamma R\int_0^{\pi/2}\left(\cos\left(\theta_e\right)_f-\cos\left(\theta_e\right)_r\right)\cos\phi\, d\phi$$

Cosine of the contact angle vs. Position



Driving force



Hydrodynamic force

- Assumptions

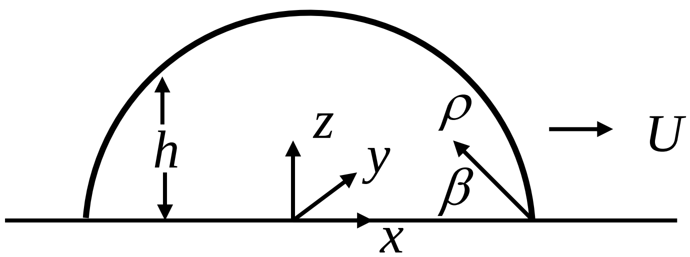
1. Incompressible isothermal Newtonian flow in the liquid with a constant viscosity.
2. Reynolds number is assumed to be negligibly small so that inertia effects can be ignored.
3. The capillary and Bond numbers are assumed sufficiently small that the shape of the drop is negligibly influenced by motion and by gravity, respectively.

Two approaches to estimate the hydrodynamic resistance are discussed

Wedge approximation

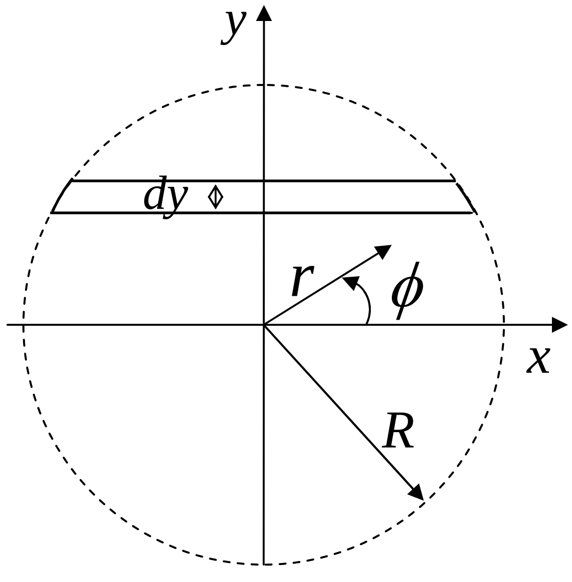
- Cox (1986) asymptotic solution for Stokes flow.

$$\boldsymbol{\tau}_{\beta\rho} = -\mathbf{i}_\rho\,\mu\left(\frac{1}{\rho}\frac{\partial \mathrm{v}_\rho}{\partial \beta}\right)_{\beta=0} = -\mathbf{i}_\rho\,2\mu U\left(\frac{E}{\rho}\right)$$



$$\rho = \sqrt{R^2 - y^2} - x \qquad E = \frac{\sin^2\theta_w}{\sin\theta_w\cos\theta_w - \theta_w}$$

$$\boldsymbol{\tau}_w(x,y) = \mathbf{i}_x\,2\mu U\frac{\sin^2\theta_w}{(\sin\theta_w\cos\theta_w - \theta_w)\left(\sqrt{R^2-y^2}-x\right)}$$



$$F_h = \int_\Omega \tau_w(x,y)\,d\Omega$$

Wedge approximation (contd.)

$$\tan\theta_w = \tan\theta \, \cos\phi \qquad \tan\theta_w = A\sqrt{1-\frac{y^2}{R^2}}$$

$$F_h = 8\mu UR \int_0^{1-\varepsilon} \frac{A^2\left(1-Y^2\right)}{\left[A\sqrt{1-Y^2}-\left(1+A^2\left\{1-Y^2\right\}\right)\tan^{-1}\left(A\sqrt{1-Y^2}\right)\right]}\left[\frac{1}{2}\ln\left(1-Y^2\right)-\ln\varepsilon\right]dY$$

$$= 8\mu UR \, f\left(\theta,\varepsilon\right)$$

where, $\varepsilon = \dfrac{L_s}{R}$

Lubrication theory

- An additional assumption is made that $\left(h_0 / R\right) \ll 1$ where h_0 is a characteristic length scale representing the height of the drop.
- The solution for the velocity distribution can be obtained as

$$v_x = -U\left(1 - 3\frac{z}{h} + \frac{3}{2}\frac{z^2}{h^2}\right)$$

$$\tau_w\left(x, y\right) = -\ \mu\frac{\partial v_x}{\partial z}\left(x, y, 0\right) = -\ 3\mu\frac{U}{h\left(x, y\right)}$$

$$h\left(x, y\right) = \sqrt{R^2 \operatorname{cosec}^2\theta - r^2}\ -\ R\cot\theta$$

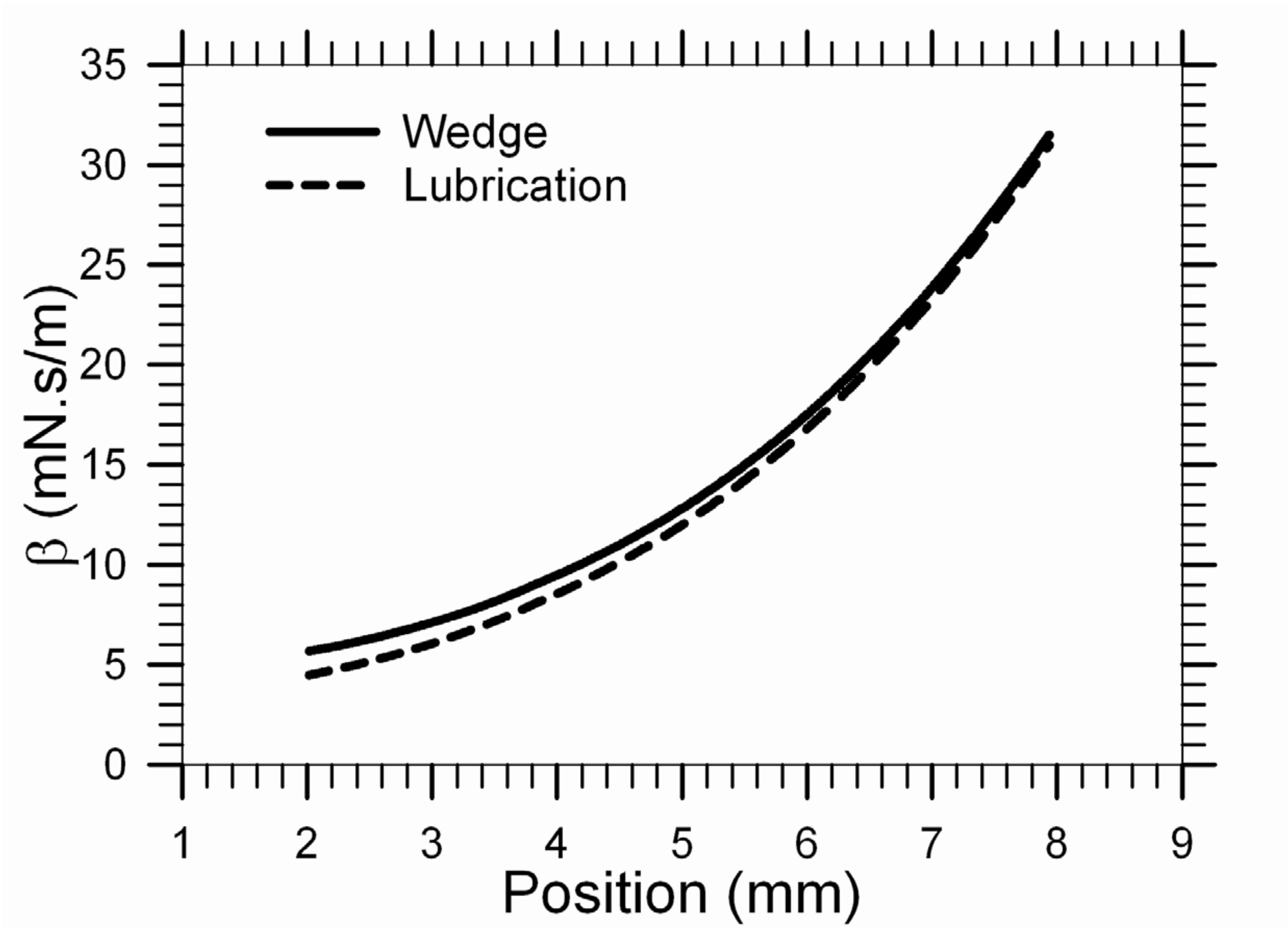
Lubrication theory (contd.)

$$F_h = \int_{\Omega} \tau_w(x,y)\, d\Omega$$

$$F_h = -\,6\pi\mu U \int_0^{R(1-\varepsilon)} \frac{rdr}{h(r)} = 6\pi\mu UR\left[g(\theta,1-\varepsilon) - g(\theta,0)\right]$$

$$g(\theta,\xi) = \left[\cot\theta \ln\left(\sqrt{\operatorname{cosec}^2\theta - \xi^2} - \cot\theta\right) + \sqrt{\operatorname{cosec}^2\theta - \xi^2} - \cot\theta\right]$$

Hydrodynamic drag coefficient $F_h = \beta U$



Quasi-steady velocity

Experiments on the Motion of Drops on a Horizontal Solid Surface Due to a Wettability Gradient

Nadjoua Moumen, R. Shankar Subramanian,* and John B. McLaughlin

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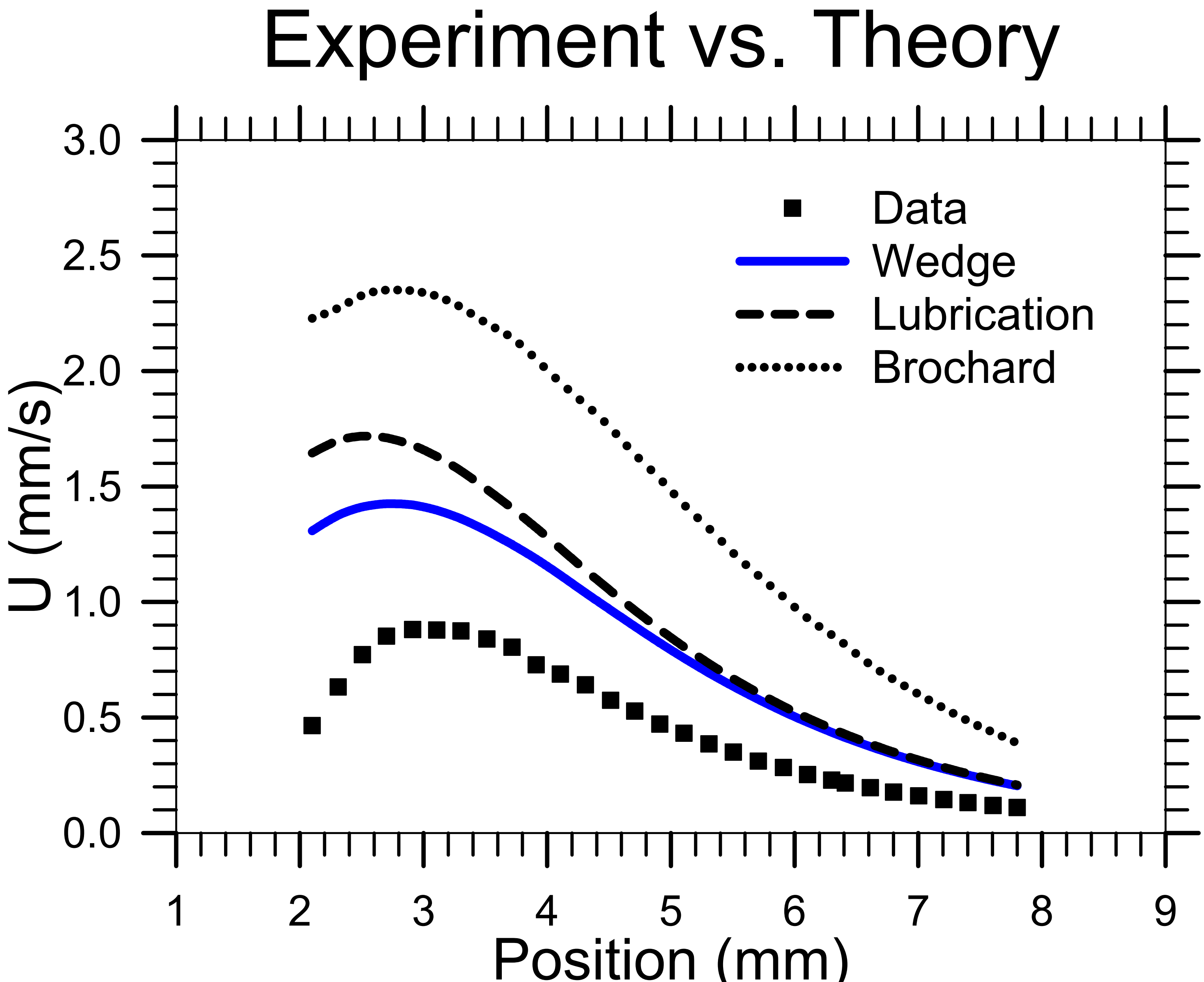
Received November 13, 2005. In Final Form: January 5, 2006

Langmuir **2006**

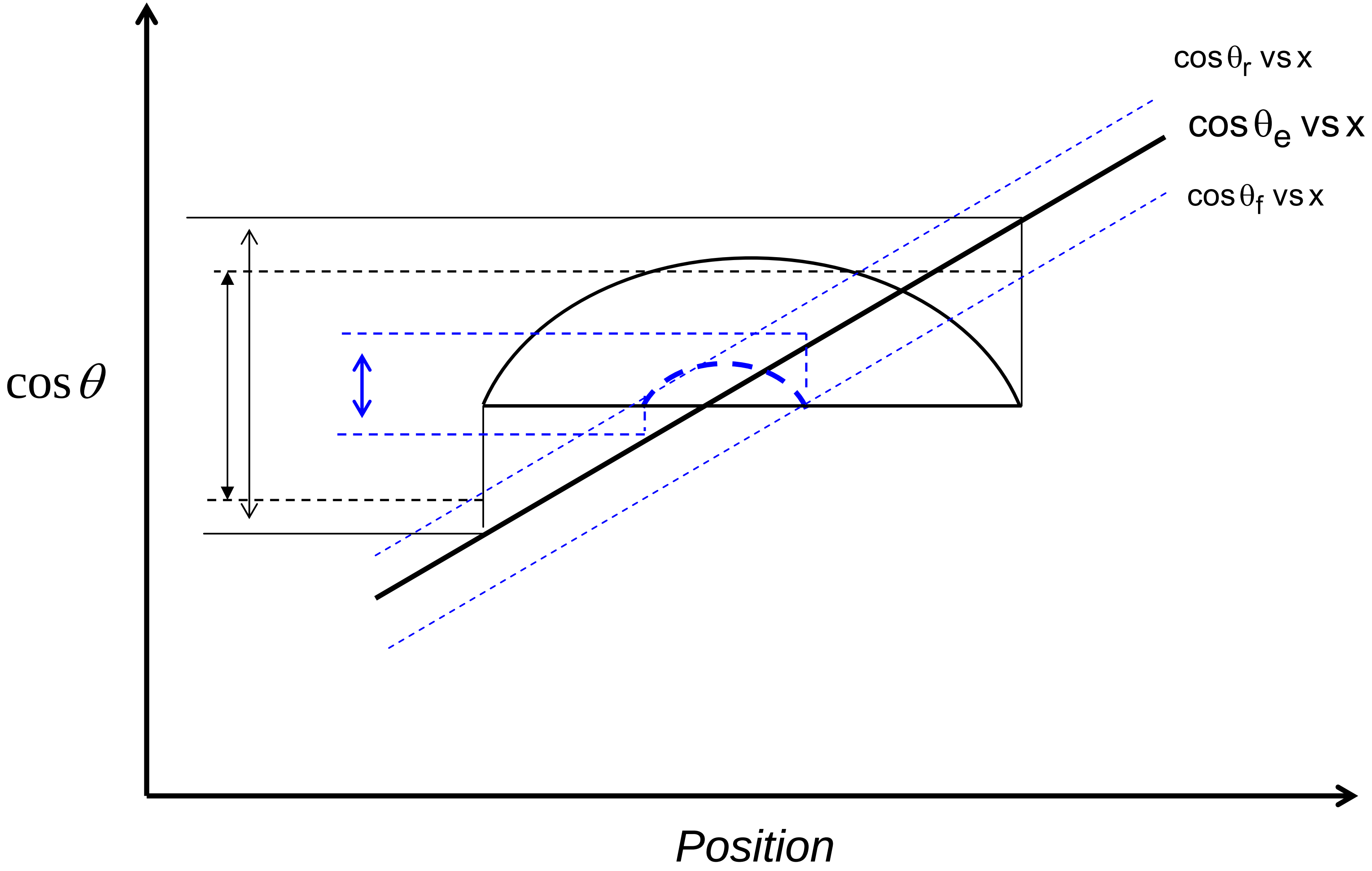

Experiment vs. Theory
Data
Wedge
Lubrication
Brochard
U (mm/s)
3.0
2.5
2.0
1.5
1.0
0.5
0.0
1
2
3
4
5
6
7
8
9
Position (mm)

Driving force with hysteresis

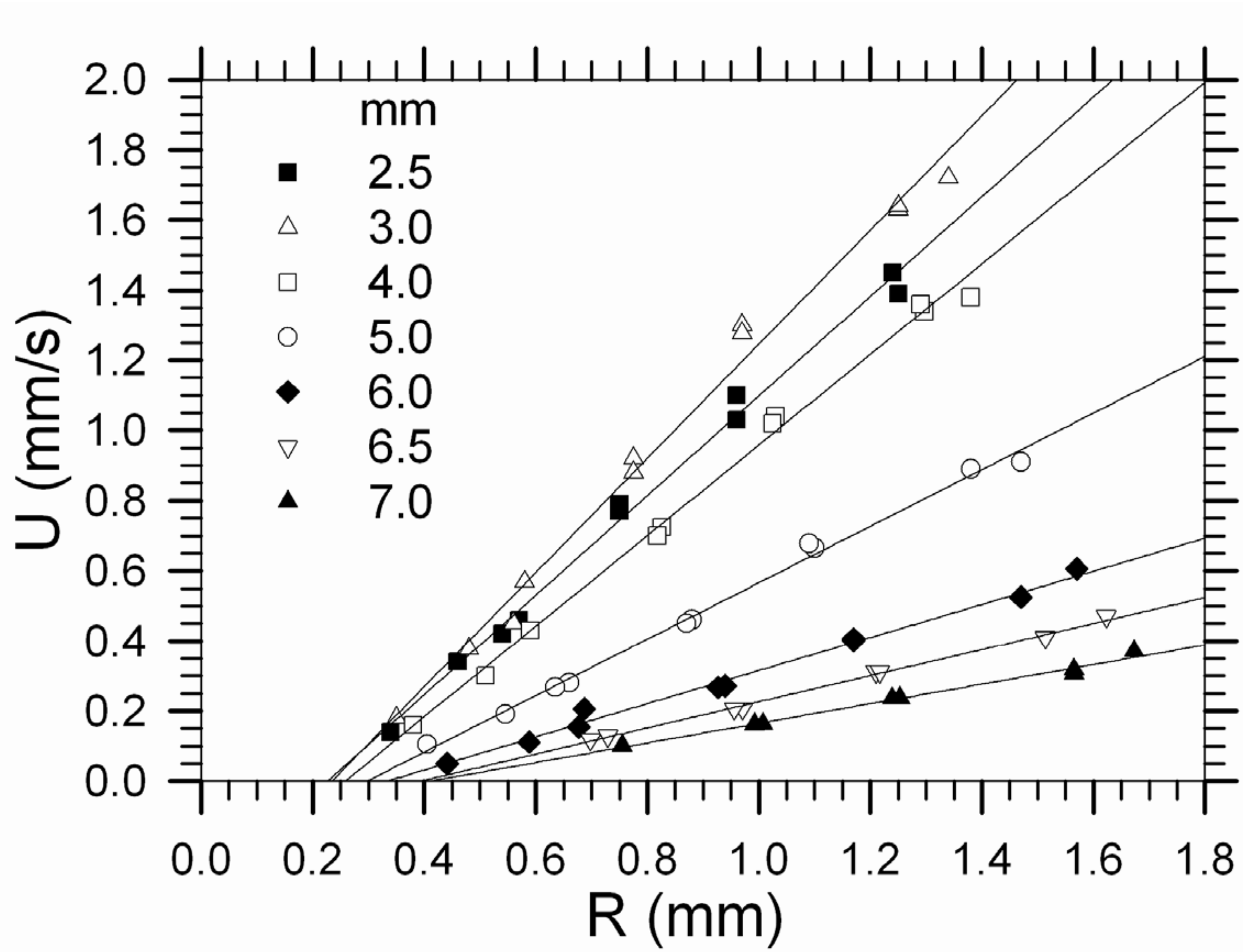
- Instead of using the equilibrium value of the contact angle around the periphery of the drop, a reduced value for the receding portion of the contact line and an increased value for the advancing portion of the contact line must be used in evaluating the driving force corrected for hysteresis.

$$F_{driving} = 2R\gamma \int_{0}^{\pi/2} \left\{ \cos\theta_f^{hys} - \cos\theta_r^{hys} \right\} \cos\phi \, d\phi$$

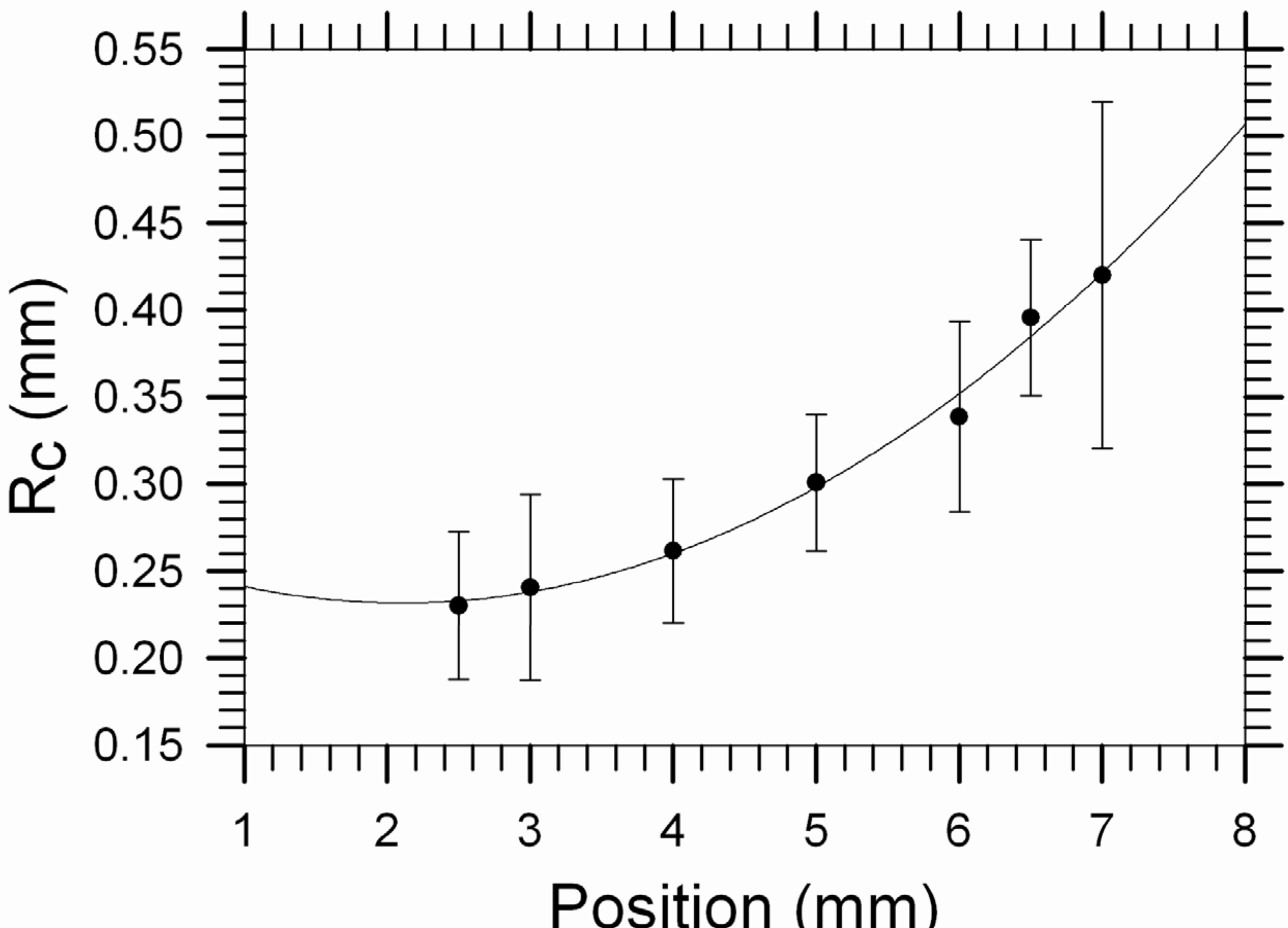
Contact angle hysteresis

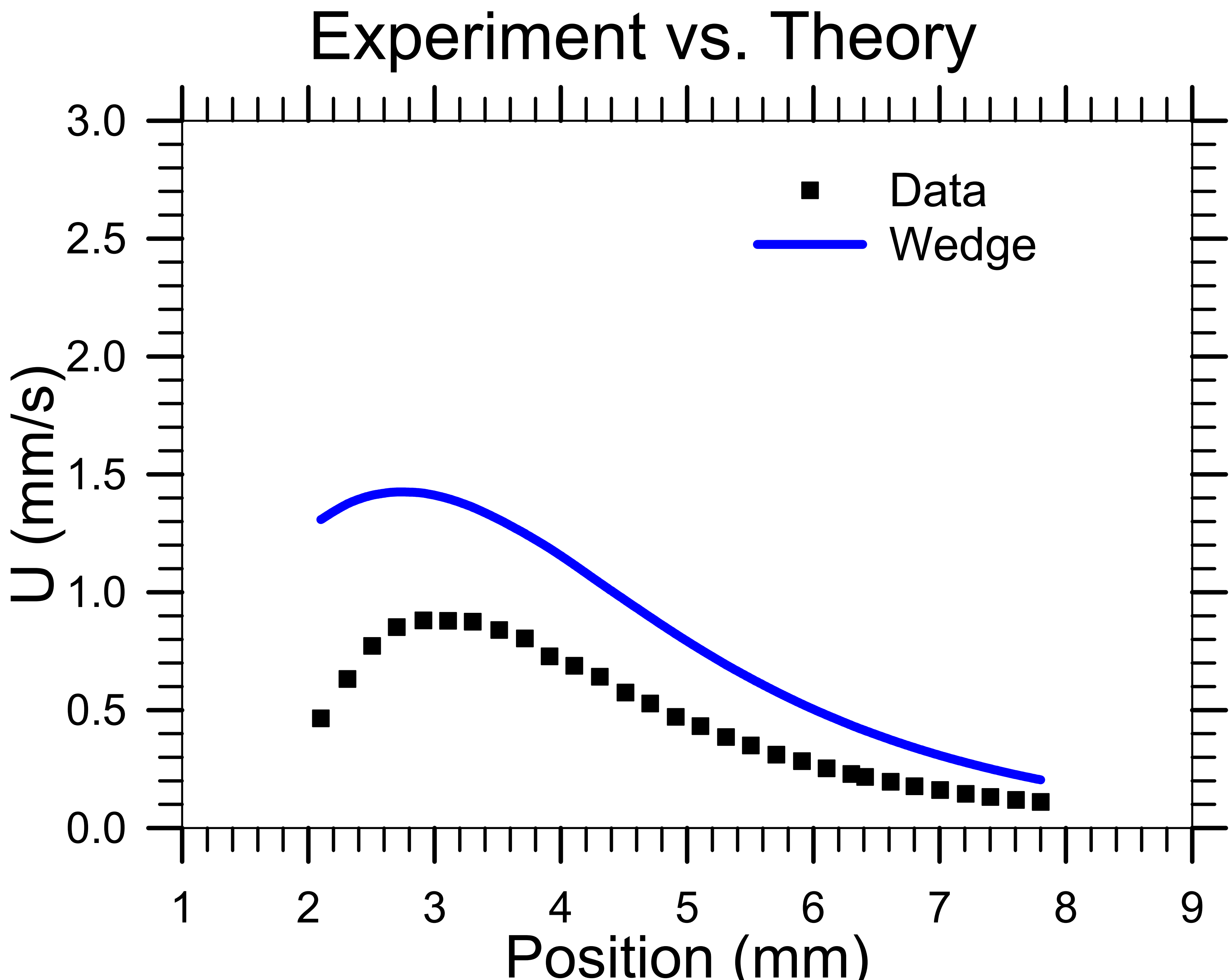


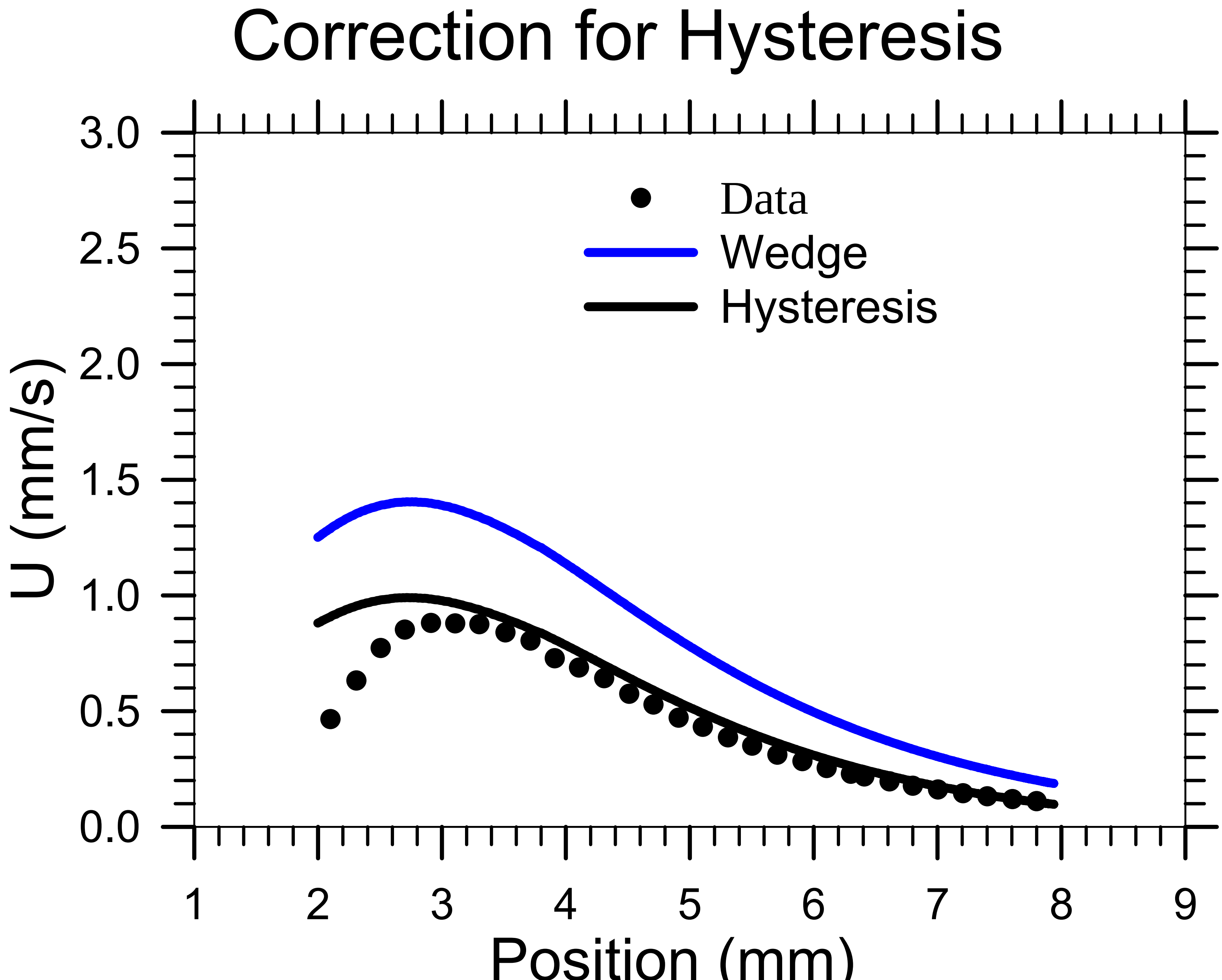
Determining the critical drop size



Critical drop size versus position

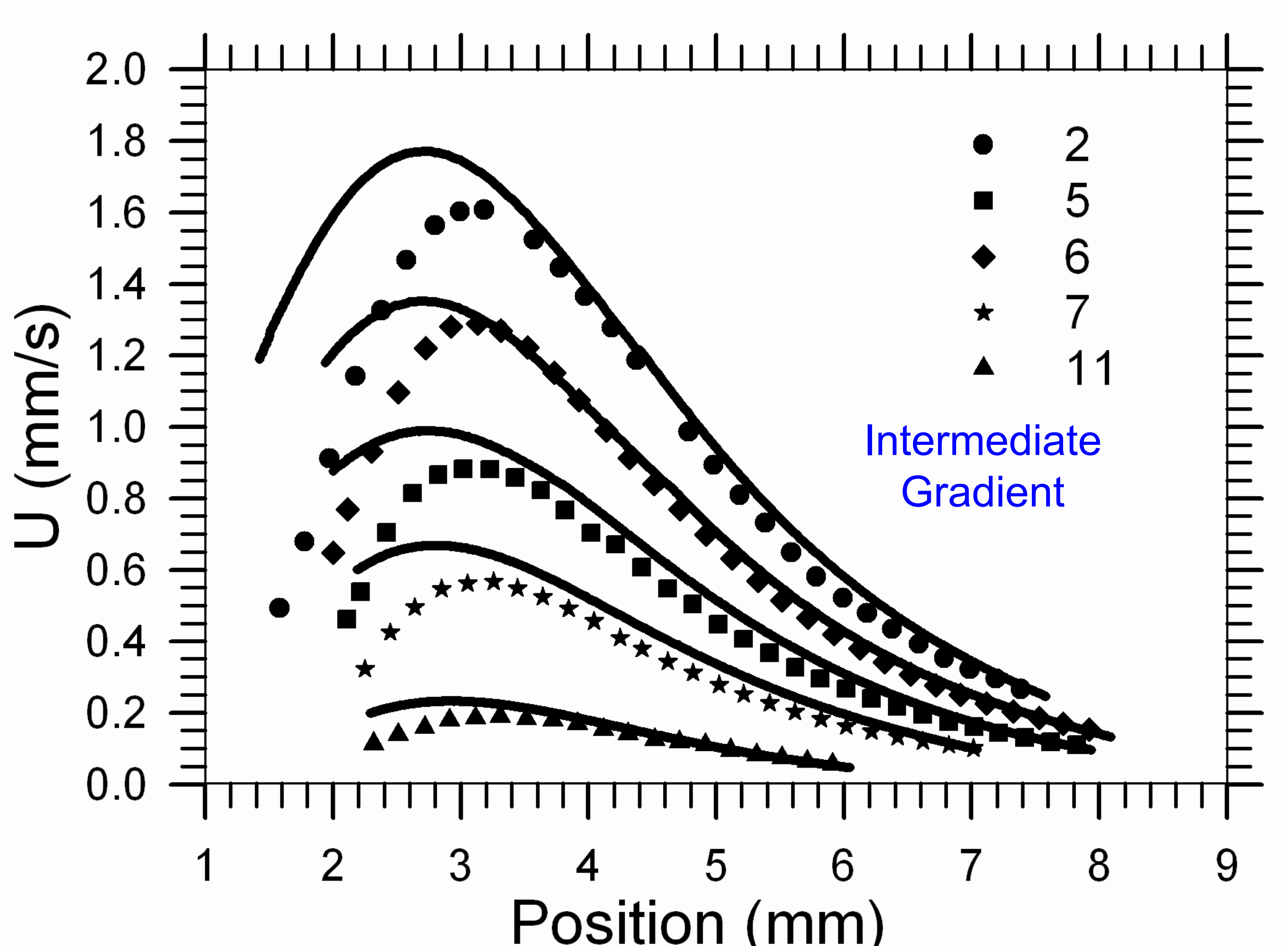



Experiment vs. Theory
Data
Wedge
U (mm/s)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
1
2
3
4
5
6
7
8
9
Position (mm)

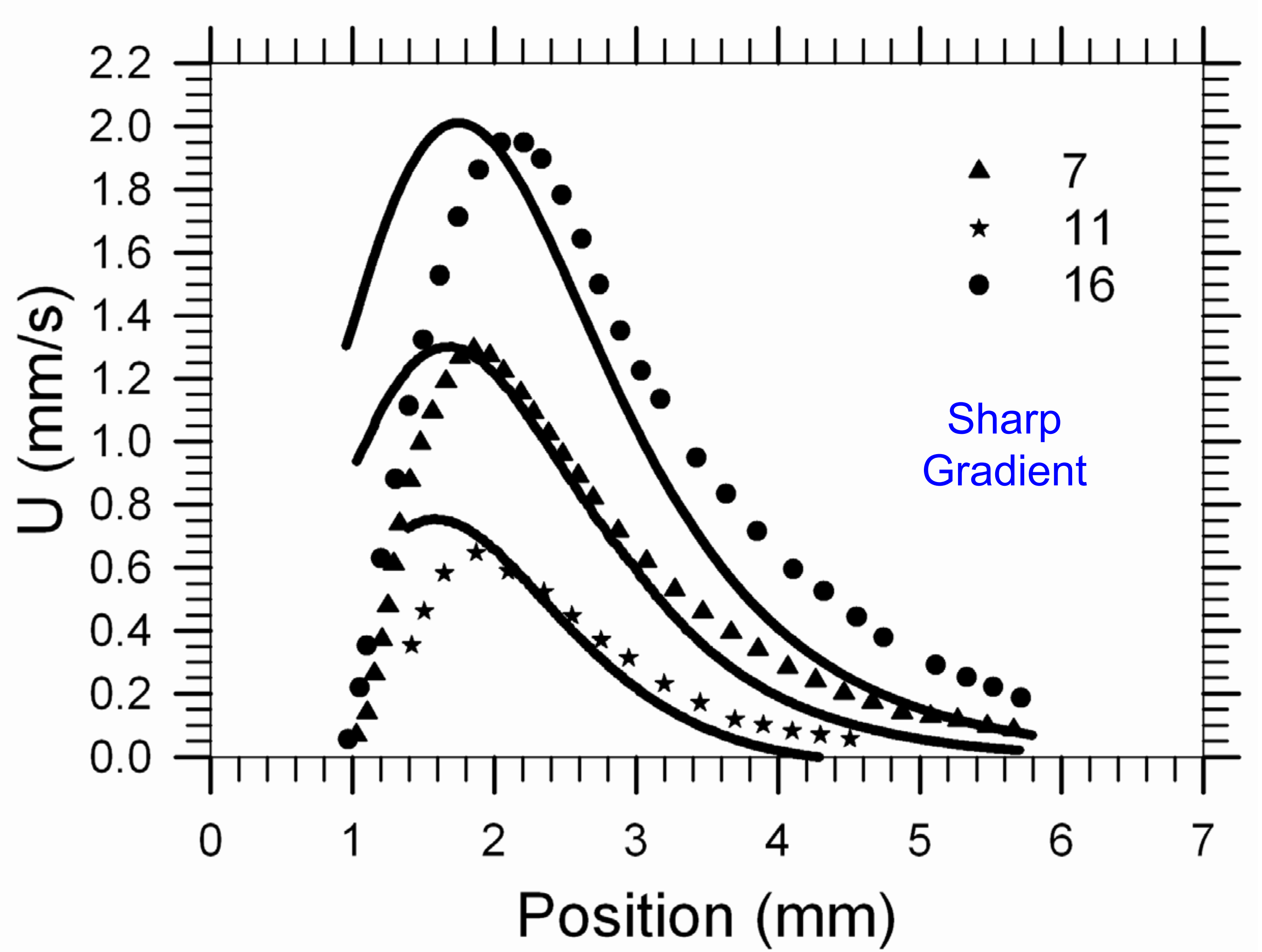


Correction for Hysteresis
Data
Wedge
Hysteresis
U (mm/s)
Position (mm)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
1
2
3
4
5
6
7
8
9

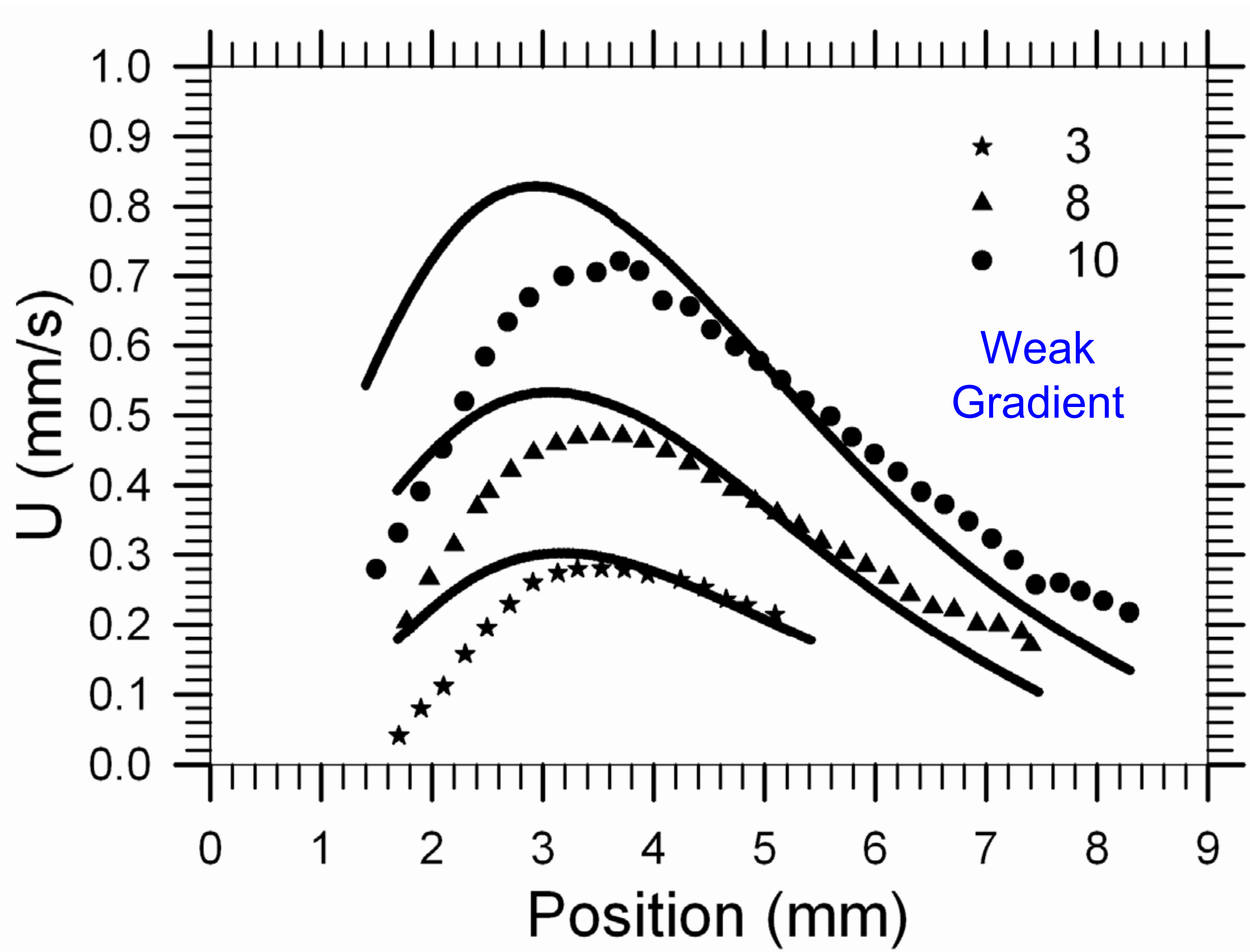
Experiment vs. Revised Predictions



Experiment vs. Revised Predictions



Experiment vs. Revised Predictions



Conclusions

- The results are reproducible.
- Measured velocities scale linearly with drop size.
- Detailed measurements of the velocity reveal the complex nature of the variation of the velocity in response to the change in driving force and in the resistance to the motion of the drop along the gradient.

Conclusions

- It is possible to interpret and organize the results using a simple hydrodynamic model in which inertial effects and deformation due to gravity as well as motion are neglected.
- The predictions from the wedge approximation describe the qualitative features of the shape of the curve of velocity versus position along the gradient surface.
- The quantitative differences are mostly accommodated by approximately accounting for the influence of hysteresis on the motion of the drops.

Acknowledgments

- National Aeronautics and Space Administration
- Professor Manoj K. Chaudhury and Dr. Susan Daniel, Lehigh University