Resonant Oscillations of Liquid Marbles

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Overview

1. Vibrations of Sessile Droplets

- Spherical and sessile droplets
- Type 1 and Type 2 modes
- Model vibrations

2. Liquid Marbles

- Concept: Perfect non-wetting droplets
- Mobility: Zero contact angle hysteresis
- Size dependence: Spherical to puddle

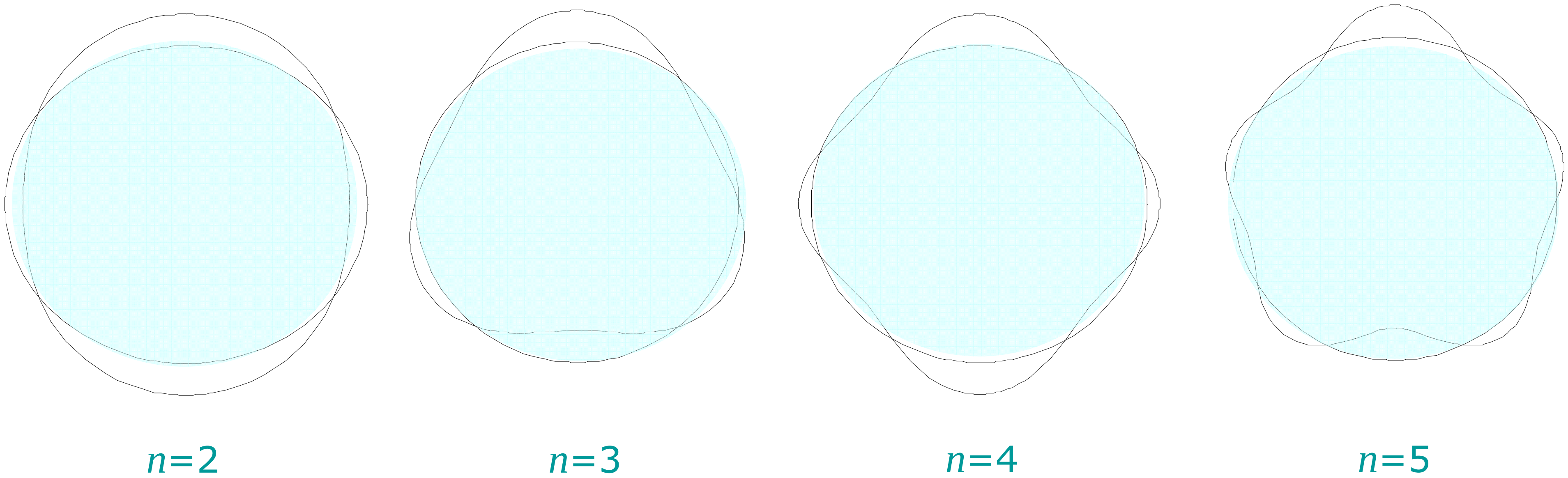
3. Oscillation Experiments

- Experimental set-up
- Spectra
- Volume and mode dependence

Vibration of Sessile Droplets

Vibrations of Spherical Droplets

Shape Modes



Number of nodes = 2n

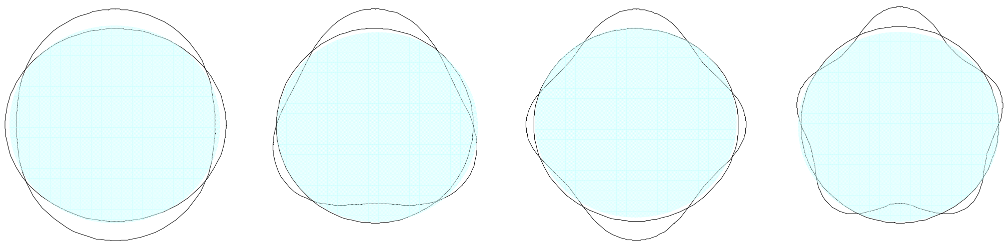
Resonant Frequencies

$$f_n^2 = \frac{n(n-1)(n+2)\gamma_{LV}}{4\rho\pi^2 R^3} \rightarrow \frac{n^3\gamma_{LV}}{3\pi\rho V}$$

Reference: Lamb, H., *Hydrodynamics*, Cambridge University Press (1932).

Gravity-Capillary Waves

Wavelengths



n=2 n=3 n=4 n=5

n wavelengths fitted around perimeter (stationary surface waves)

$$p = 2\pi R = n\lambda_n$$

1-D Dispersion Equation

Bath of depth h, wave vector $q=2\pi/\lambda$

γ_{LV} is surface tension and ρ is density

$\omega=2\pi f$ is angular frequency

$$\omega^2 = \left(gq + \frac{\gamma_{LV} q^3}{\rho} \right) \tanh(qh)$$

gravity

surface tension

finite depth

$$\omega_n^2 \approx \frac{\gamma_{LV} q_n^3}{\rho} = \frac{\gamma_{LV} (2\pi)^3}{\rho \lambda_n^3} \xrightarrow[2\pi R = n\lambda_n]{} f_n^2 \approx \frac{n^3 \gamma_{LV}}{4\rho\pi^2 R^3} = \frac{n^3 \gamma_{LV}}{3\pi\rho V}$$

Sessile Droplets

Effect of Substrate

1. Breaks complete spherical shape

   Small droplets are spherical caps

   Larger droplets flatten and have gravitational effects

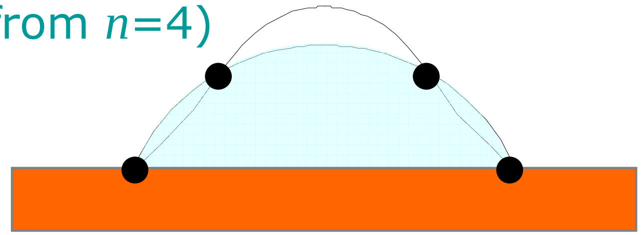
   $\Rightarrow$ *Introduces dependence on contact angle, θ, and volume, V*

2. Contact line imposes boundary conditions

   $\Rightarrow$ *Introduces dependence on contact angle hysteresis, $\Delta\theta$*

Type 1 – Immobile Contact Line

j=2 (from n=4)



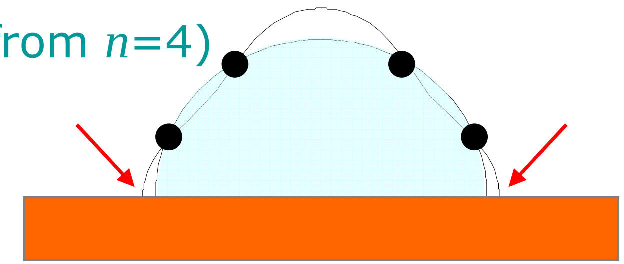
Number of nodes = 2j

Nodes at contact line

Constant contact diameter

Type 2 – Mobile Contact Line

k=2 (from n=4)



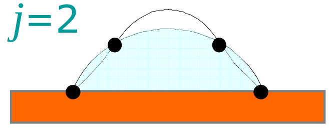
Number of nodes = 2k

Anti-nodes at contact line

Constant contact angle, θ_e

Reference: Noblin, X. *et al.*, Eur. Phys. J. E 14 (2004) 395-404.

Type 1 – Immobile Contact Line



Pseudo-wavelength

Fit (j+1) half-wavelengths around perimeter length, p: $2p = (j+1)\lambda_j$

Perimeter length depends on droplet volume and contact angle, $p=p(V,\theta_e)$

Substitute into dispersion equation:

$$f_j^2 = \frac{(j+1)g}{4\pi p}\left(1+\left(\frac{(j+1)\pi}{p\kappa}\right)^2\right)\tanh\left(\frac{(j+1)\pi h}{p}\right)$$

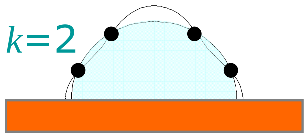
where $\kappa^{-1}=(\gamma_{LV}/\rho g)^{1/2}$ is the capillary length

Noblin *et al* suggest mean height of droplet be used for depth, $h_m=V/\pi R^2$

Limits

Capillary regime:	$f \propto (j+1)^{3/2}$	3/2 power law for mode
Gravity regime:	$f \propto (j+1)$	linear dependence on mode

Type 2 – Mobile Contact Line



Pseudo-wavelength

Fit k wavelengths around perimeter length, p: $$p = k\lambda_k$$

Perimeter length depends on droplet volume and contact angle, $p=p(V,\theta_e)$

Substitute into dispersion equation:

$$f_k^{\,2} = \frac{kg}{2\pi p}\left(1+\left(\frac{2\pi k}{p\kappa}\right)^2\right)\tanh\left(\frac{2\pi hk}{p}\right)$$

Limits

Capillary regime: $f \propto k^2$ 3/2 power law for mode

Gravity regime: $f \propto k$ linear dependence on mode

Mixed modes

Pure type 2 is difficult to study

High amplitude excitation and contact angle hysteresis can lead to both contact line motion and contact angle oscillating simultaneously

Liquid Marbles

Experimental Design

Requirements

1. For approximation to sphere, need very large (>>90°) contact angles
2. For type 2 mobile contact lines, need very low contact angle hysteresis

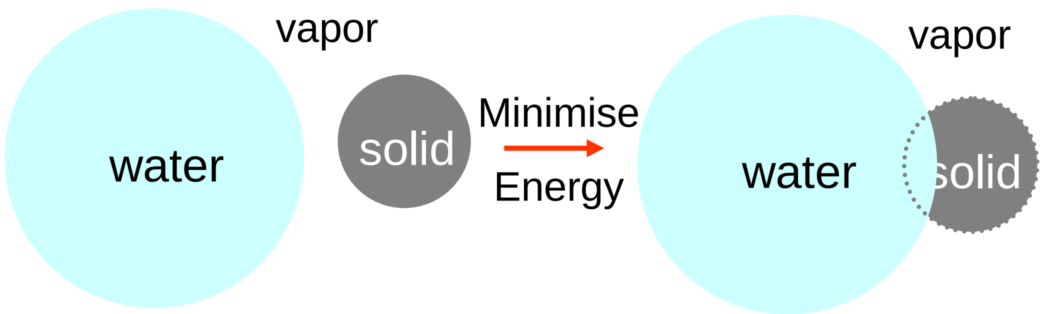
$\Rightarrow$ Lithographically fabricated superhydrophobic surface?

Problem in obtaining mobile contact lines

Instigation of Cassie-Baxter to Wenzel transition

OR use liquid marbles on Teflon AF1600/metal coated glass substrate

Surface free energy favors hydrophobic grains to attach to liquid-vapor interface



$$\Delta F = -\pi R_g^2 \gamma_{LV} (1 + \cos\theta_e)^2$$

Energy is always reduced on grain attachment

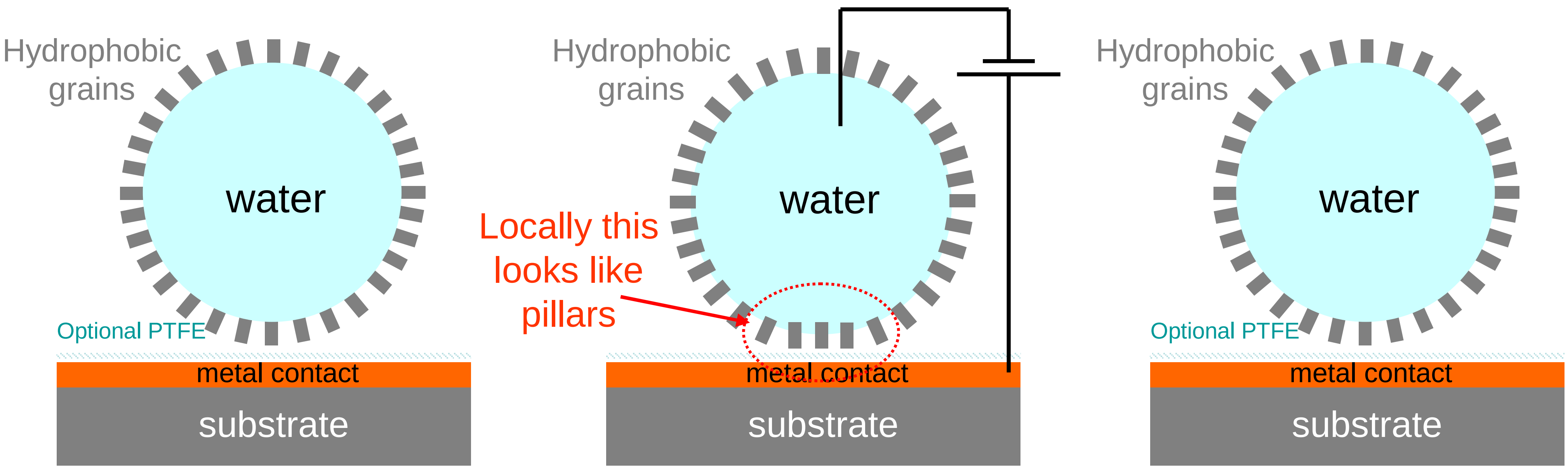
Reference Aussillous, P.; Quéré, D. Nature 411 (2001) 924-927.

Liquid Marbles as Superhydrophobic Surfaces

Reversibility Idea

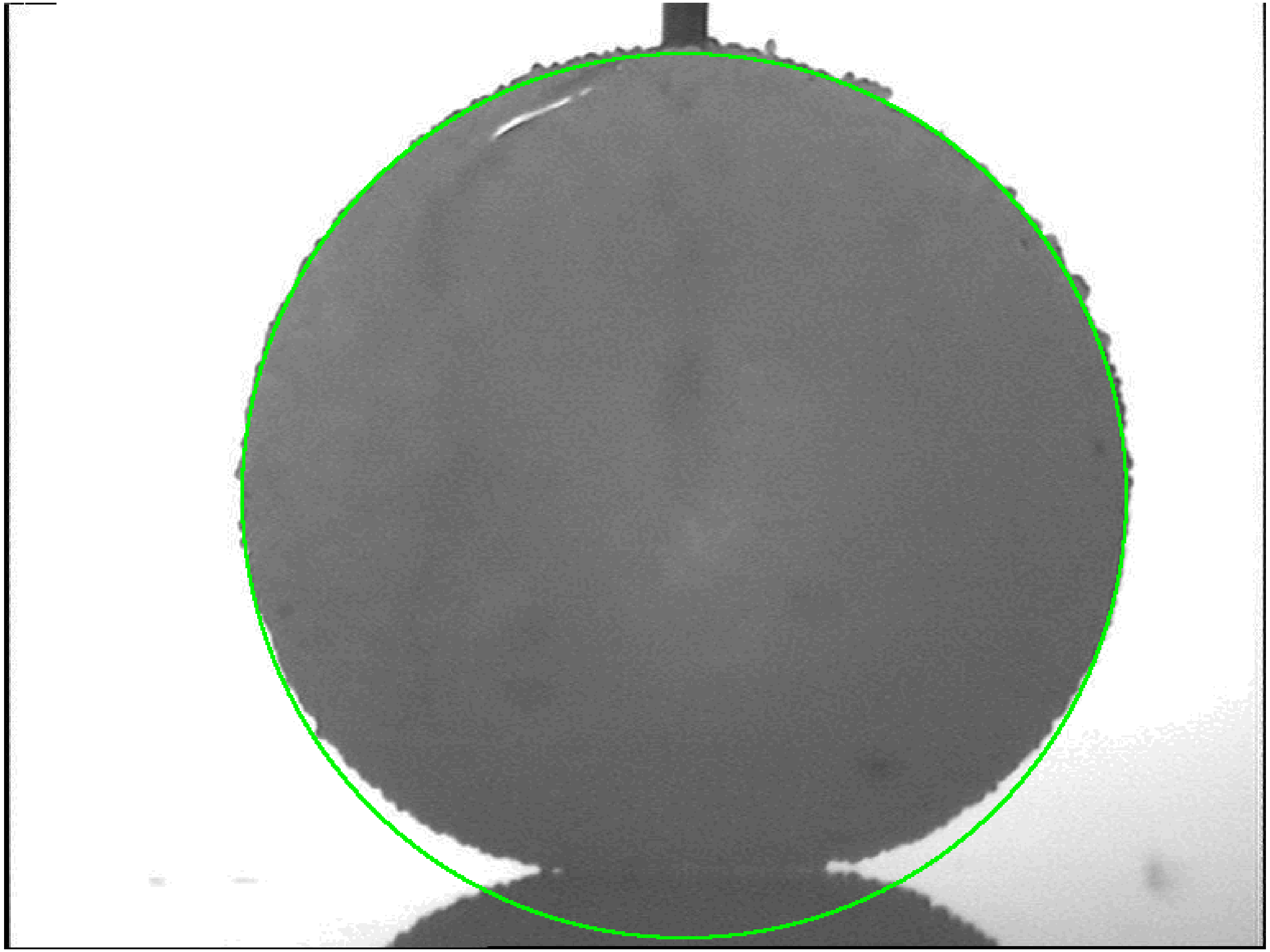
- Make the solid "pillars" adhere more to the liquid than the substrate
- Provides insulating "pillars" conformal to the liquid shape
- More hydrophobic grains "stick out" further (= to taller pillars)
- Spin coated Teflon AF1600 on substrate to stop complete breakthrough if powder/granular coating is breached

Initial Shape | Apply Voltage | Remove Voltage



Reference McHale, G.; *et al.*, Langmuir 23 (2007) 918-924.

Reversibility – Low V Cycle



Mobility of Liquid Marbles

Hydrophobic lycopodium marbles are highly mobile

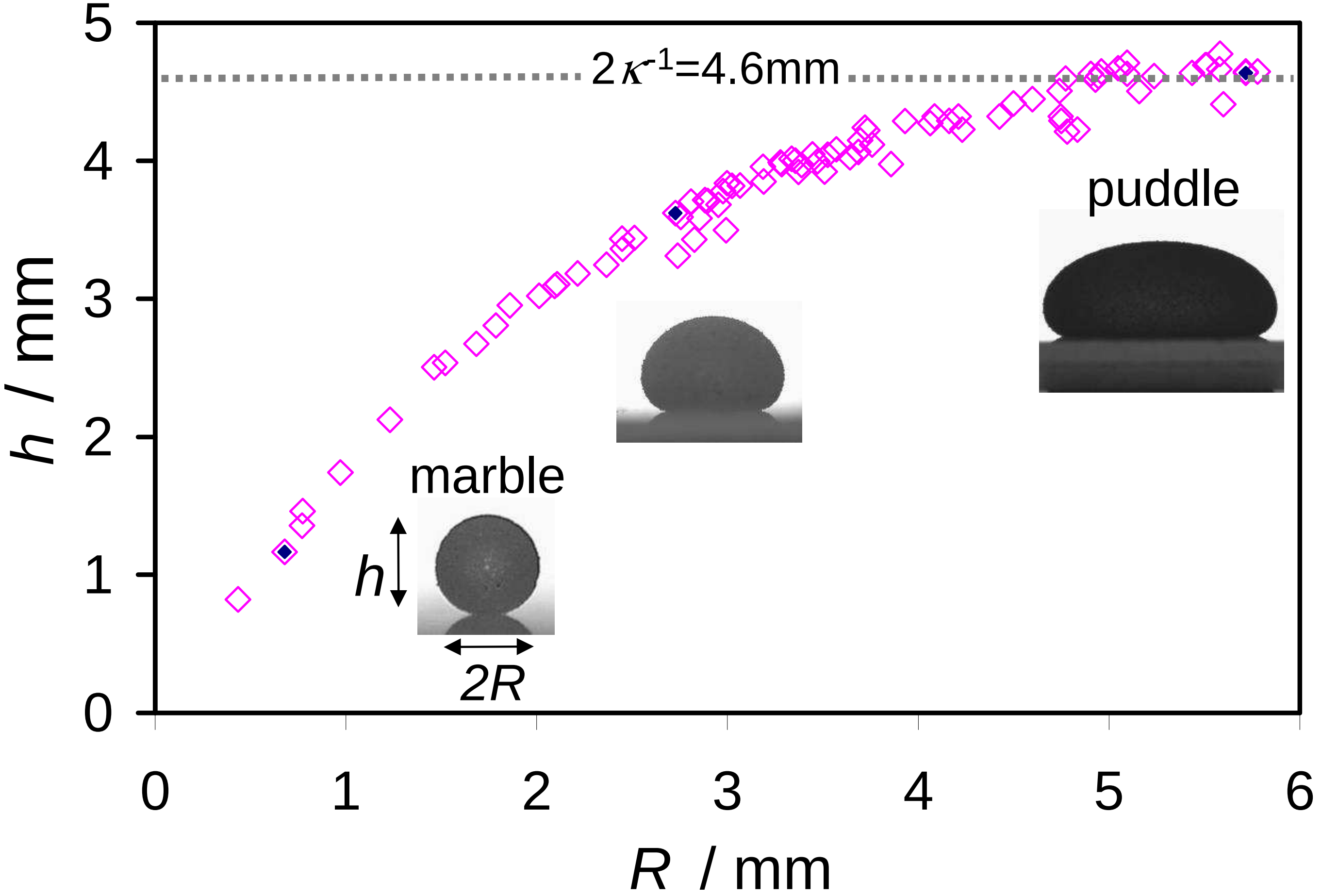
Gravity distorts shape from spherical as volume increases

Liquid Marbles – Size Data

Hydrophobic lycopodium plus 0.01M KCl deionised water

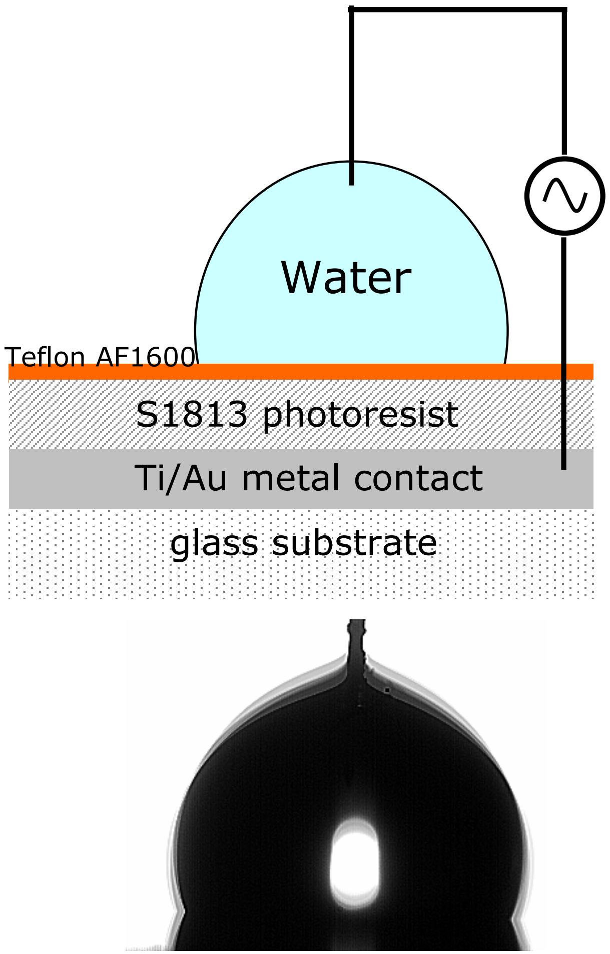
Transition from marble to puddle with increasing volume

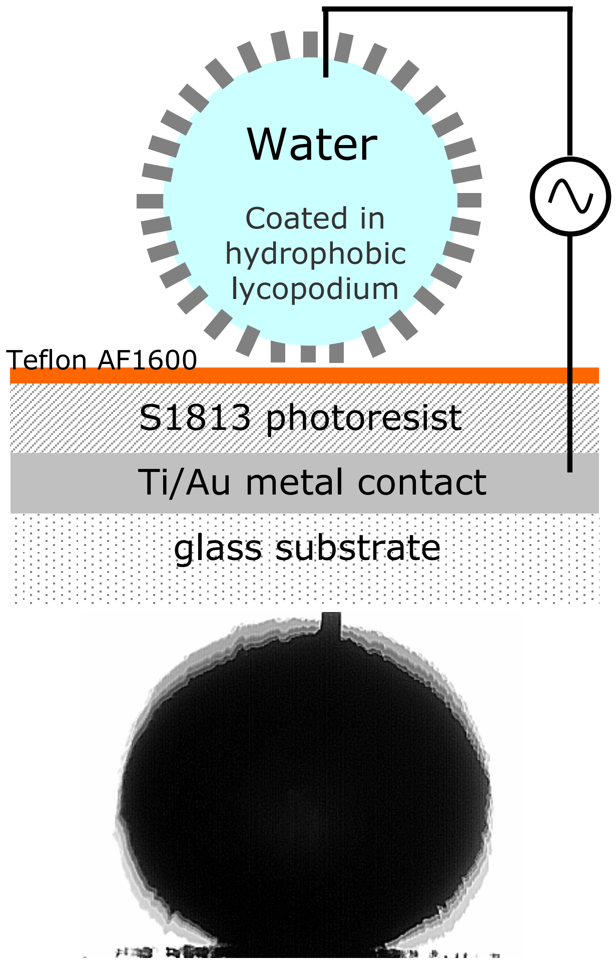
Limiting value of puddle height gives twice the capillary length, $h=2\kappa^{-1}$



Oscillation Experiments

Experimental Arrangements





0.01M KCl, ~5 μl, 100 V, 44 Hz   0.01M KCl, 5 μl, 100 V, 39 Hz

Hydrophobic lycopodium (17 ±3) μm, 5-275 μl droplets of 0.01M KCl deionised water. Up to 200V p-p, 1 Hz-250 Hz sweep. High speed camera

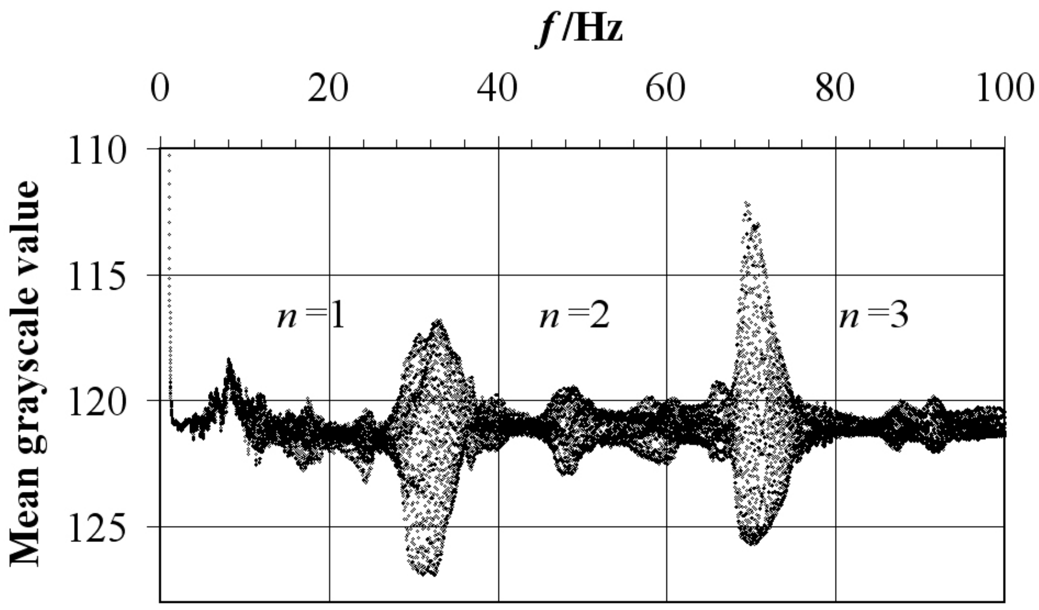
Reference For EWOD applied to sessile droplet oscillations, see recently published paper: Min Oh, J.; *et al*. Langmuir 24 (2008) 8379-8386.

Example Data

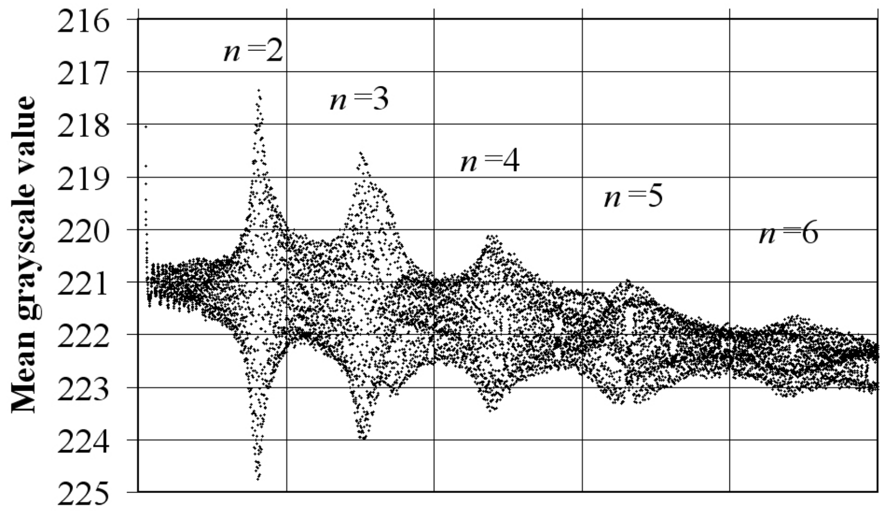
Example of the z-axis profile data used to locate resonant frequencies (0-100Hz)

Mean greyscale value within a rectangular box selection at an anti-node close to the electrode wire for 100 µl volumes

Droplet

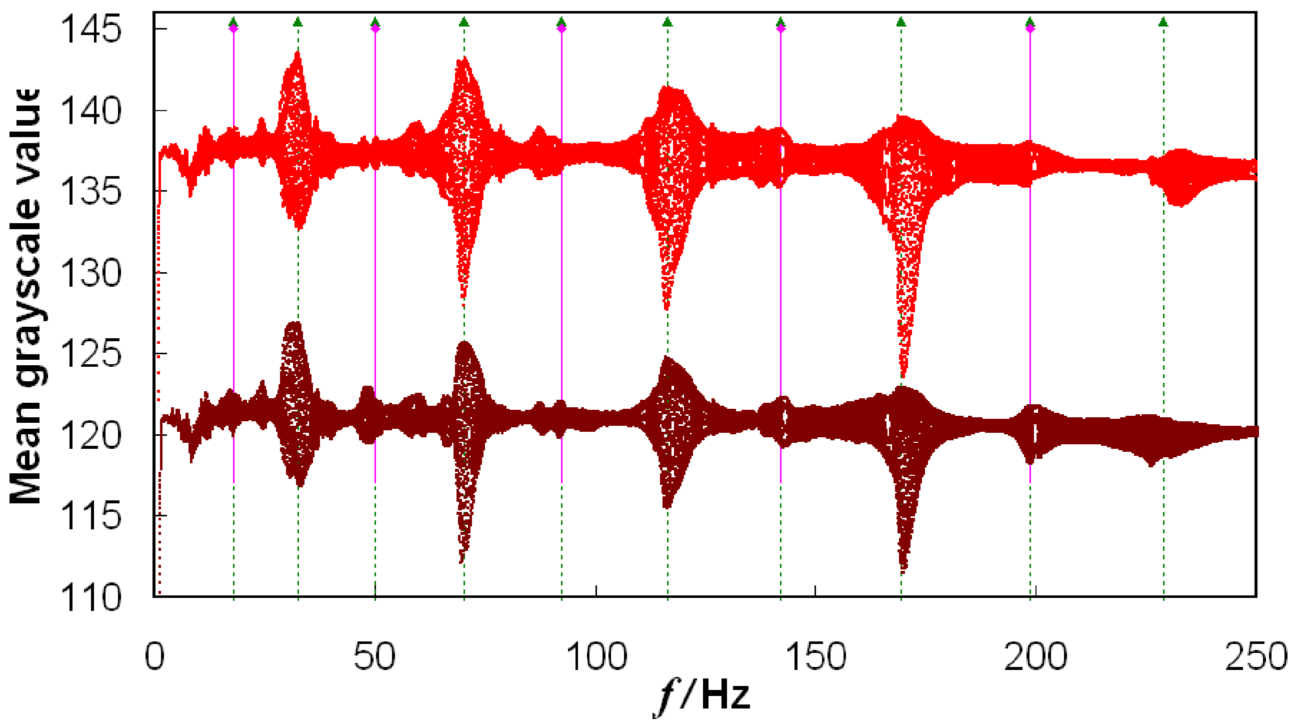


Liquid Marble



Analysis of 100 μl Sessile Droplet

Fits using ρ=997 kg m^{-3}, γ_{LV}=72.8 mN m^{-1}. Single fitting parameter used is θ_e to reduce perimeter length, p, by 7% (modified from 115° to 87°) to achieve a fit



Data from RHS of wire

Data from LHS of wire

Immobile contact line case: green (j=1, 2, … 10) (capillary only with tanh()=1)

Mobile contact line case: pink (k=1, 2, … 5) (capillary only with tanh()=1)

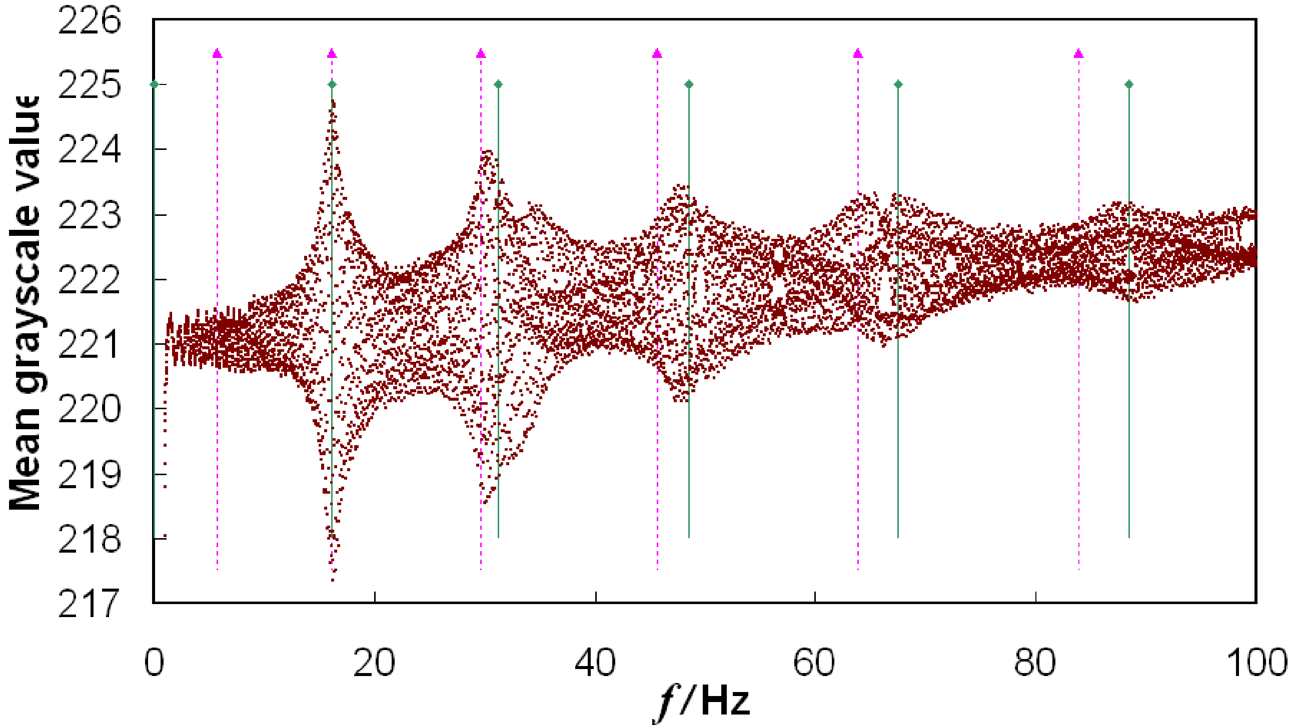
Major resonances occur for immobile contact line case with mode number j even

Resonances with j odd are reduced. These correspond to contact line having either node or anti-node, e.g. immobile j=3 and mobile k=2 both give 2λ perimeter length and same f

Preliminary Analysis of 100 μl Liquid Marble

Fits using, γ_{LV}=52 mN m^{-1} determined from spherical to puddle data

Single fitting parameter used ρ=1690 kg m^{-3} assuming spherical shape



Data from LHS of wire

Mobile contact line case: pink (j=1, 2, …, 6) (capillary only with tanh()=1)

Spherical droplet case: green (n=2, …, 6)

First major resonances occurs for n=2 and j=2 mode numbers

Spherical case using $n(n-1)(n+2)$ formula appears excellent provided an effective density is used - ratio of surface tension to effective density gives a "spring constant"

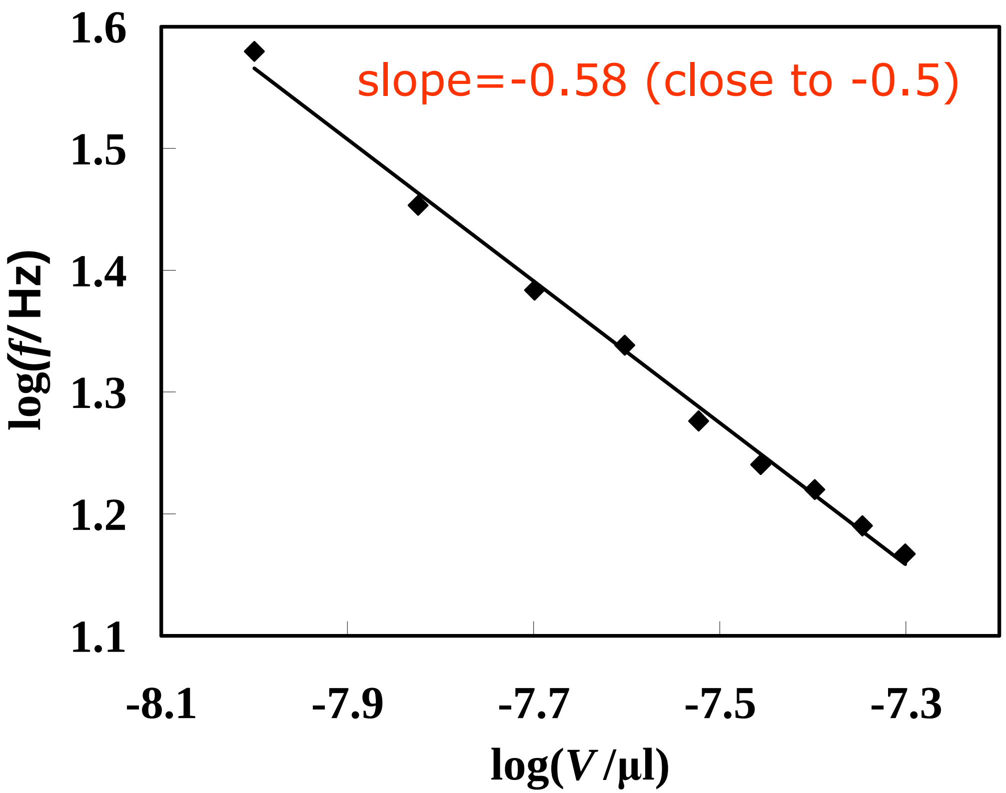
Volume Dependence (Marble)

Assuming capillary dominated

$$f_k^2 \approx \frac{2\pi k^3 \gamma_{LV}}{p^3 \rho} \tanh\left(\frac{2\pi h k}{p}\right) \propto \frac{k^3}{p^3} \propto \frac{k^3}{V}$$

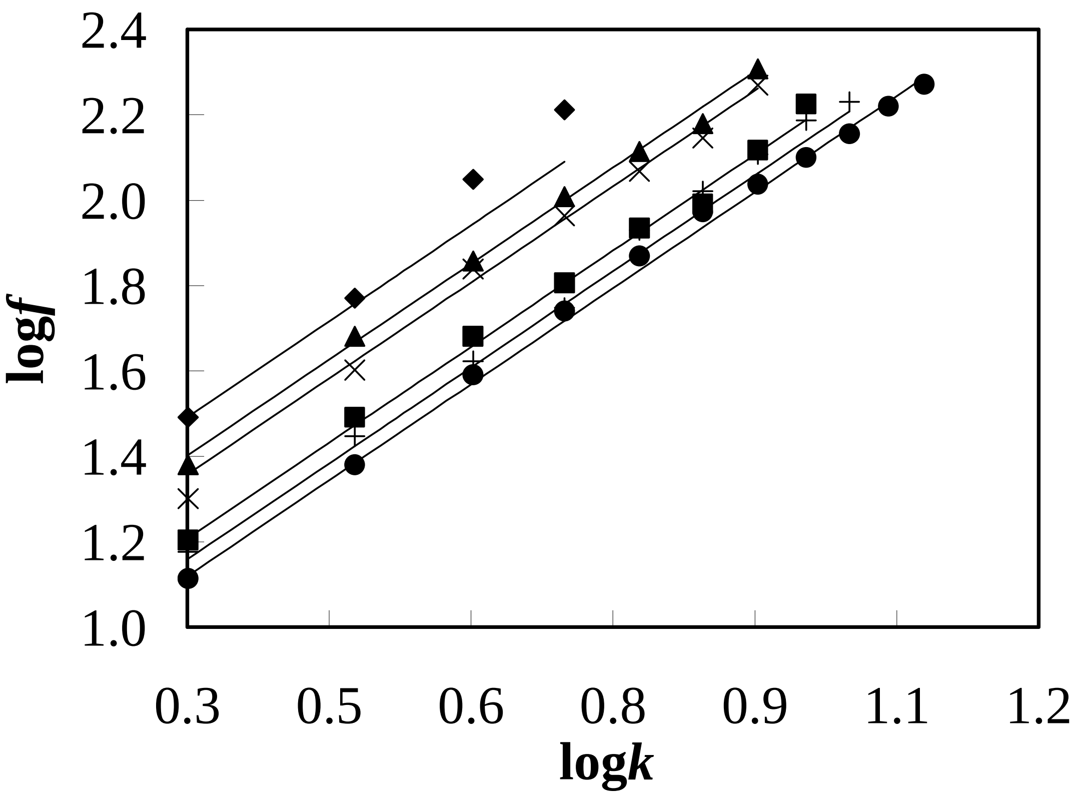
Square of frequency as a function of reciprocal of marble volume

Data for k=2 mode (V=10-50 μl)



Mode Dependence (Marble)

Log-log plot of frequency as a function of mode number for liquid marbles of volumes 10 μl (♦), 30 μl (▲), 50 μl (x), 100 μl (■), 125 μl (+), 150 μl (●).



Solid lines are fits using 52 mN m^{-1} (ρ=1690 kg m^{-3} for 50, 100, 125 and 150 μl; ρ=2300 kg m^{-3} for 30 μl; ρ=4560 kg m^{-3} for 10 μl (mode misindentification likely for 10 μl)

Fitting model: Capillary only with mobile contact line and tanh()=1

Note: Spherical model can be fitted to data using lightly adjusted density values (spring constant)

Summary

- Shape oscillations can be induced using an EWOD approach
- Droplet's main resonances for immobile contact line and j even
- Liquid marbles provide an idealized perfectly non-wetting system
- No need for active levitation/microgravity
- Zero contact angle hysteresis/mobile contact line
- Potential to study capillary-to-gravity regime transition

The End

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See Also Our Poster

Microfluidic Switchable Diffraction Grating

Gary G. Wells, ***Carl V. Brown***, *Glen McHale, Michael I. Newton and Christophe L. Trabi*

See Poster - Microfluidic Switchable Diffraction grating

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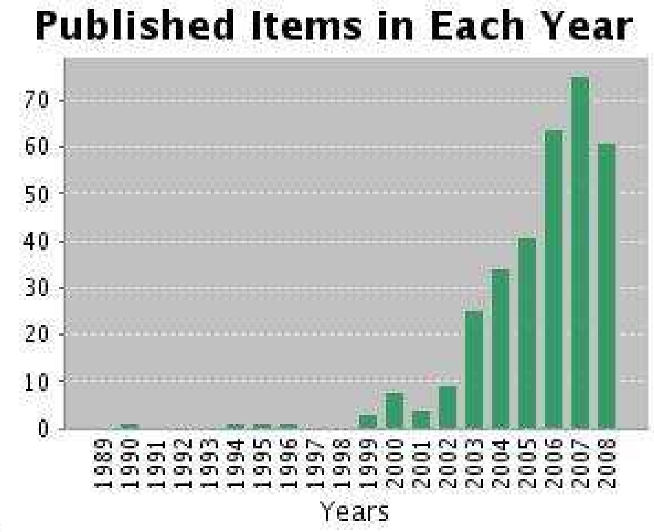
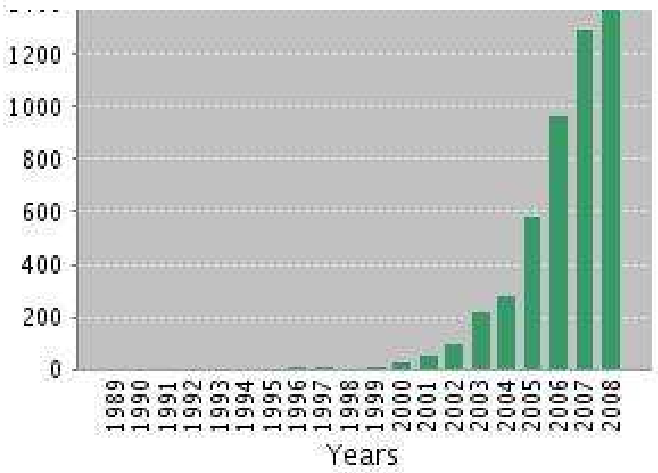
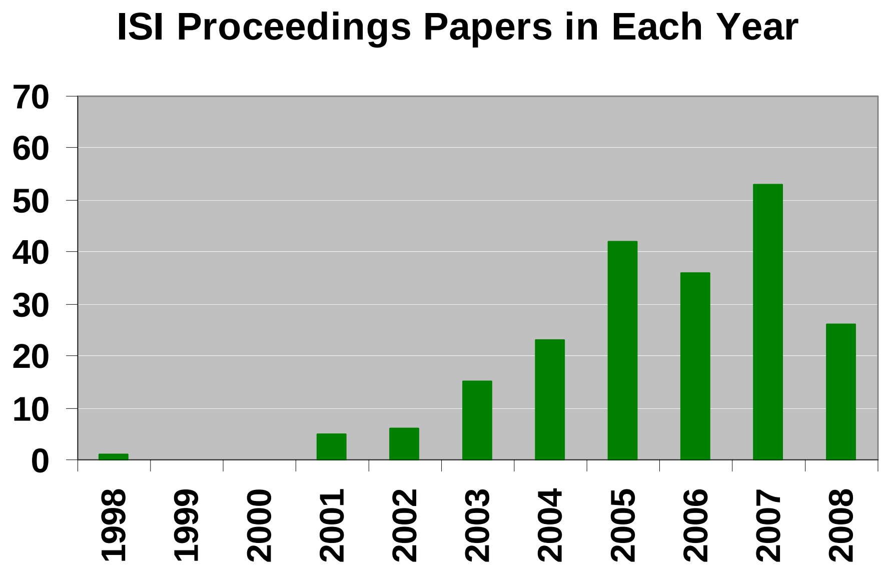
Appendices

"Electrowetting"







Fitting Equations

Type 1 – Immobile Contact Line Analysis (k=2,3,4, …)

$$f_j^2 = \frac{(j+1)g}{4\pi p}\left(1+\left(\frac{(j+1)\pi}{p\kappa}\right)^2\right)\tanh\left(\frac{(j+1)\pi h}{p}\right) \approx \frac{\pi(j+1)^3\gamma_{LV}}{4p^3\rho}$$

Sessile Droplet (side-view) Perimeter: $\text{side} - \text{view perimeter} = 2R_{cap}\theta$

$$\beta(\theta) = 2 - 3\cos\theta + \cos^3\theta \qquad R_{cap} = \left(\frac{3V}{\pi\beta}\right)^{1/3}$$

Type 2 – Mobile Contact Line Analysis (k=2,3,4, …)

$$f_k^2 = \frac{kg}{2\pi p}\left(1+\left(\frac{2\pi k}{p\kappa}\right)^2\right)\tanh\left(\frac{2\pi hk}{p}\right) \approx \frac{2\pi k^3\gamma_{LV}}{p^3\rho}$$

Type 2 – Spherical Droplet Analysis (k=2,3,4, …)

$$f_n^2 = \frac{n(n-1)(n+2)\gamma_{LV}}{4\rho\pi^2R^3} = \frac{2\pi n(n-1)(n+2)\gamma_{LV}}{p^3\rho}$$

Spherical Droplet (side-view) Perimeter: $p = 2\pi R = 2\pi\left(\frac{3V}{4\pi}\right)^{1/3}$

Sessile Droplet (side-view) Perimeter: $\text{side} - \text{view perimeter} = 2R_{cap}\theta$

$$\beta(\theta) = 2 - 3\cos\theta + \cos^3\theta \qquad R_{cap} = \left(\frac{3V}{\pi\beta}\right)^{1/3}$$

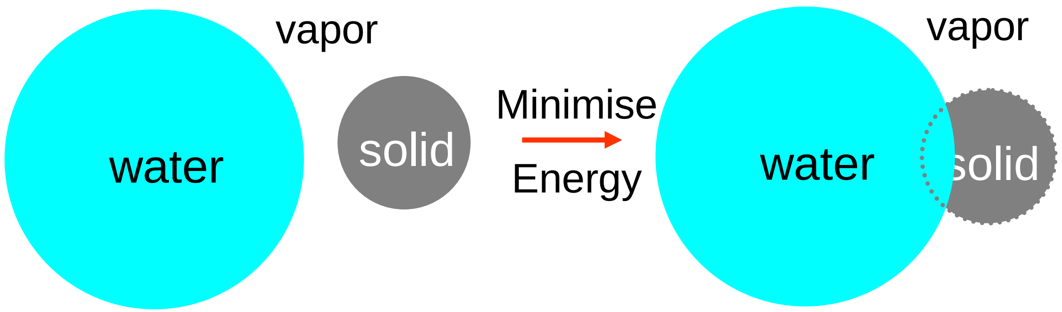
Spare Slides

Liquid Marbles

Loose Surfaces

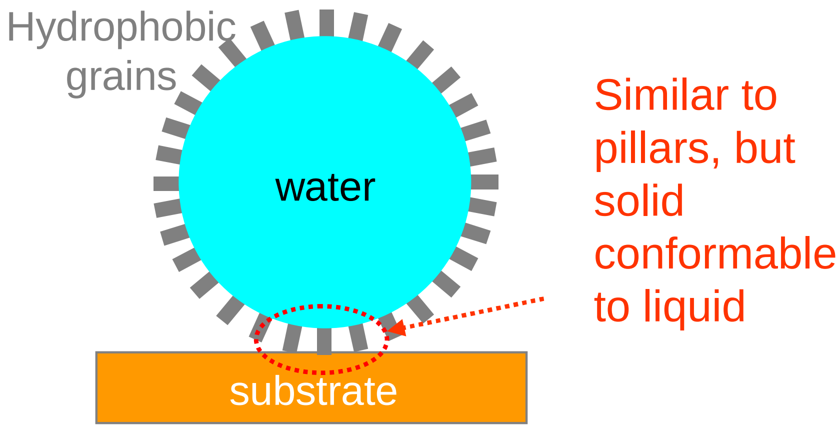
1. Grains are not fixed, but can be lifted
2. Surface free energy favors solid grains attaching to liquid-vapor interface
3. A water droplet rolling on a hydrophobic lycopodium (or other grain/powder) becomes coated and forms a liquid marble

Hydrophobic Grains and Water



$$\Delta F = -\pi R_g^{2} \gamma_{LV} (1 + \cos\theta_e)^2$$

Energy is always reduced on grain attachment



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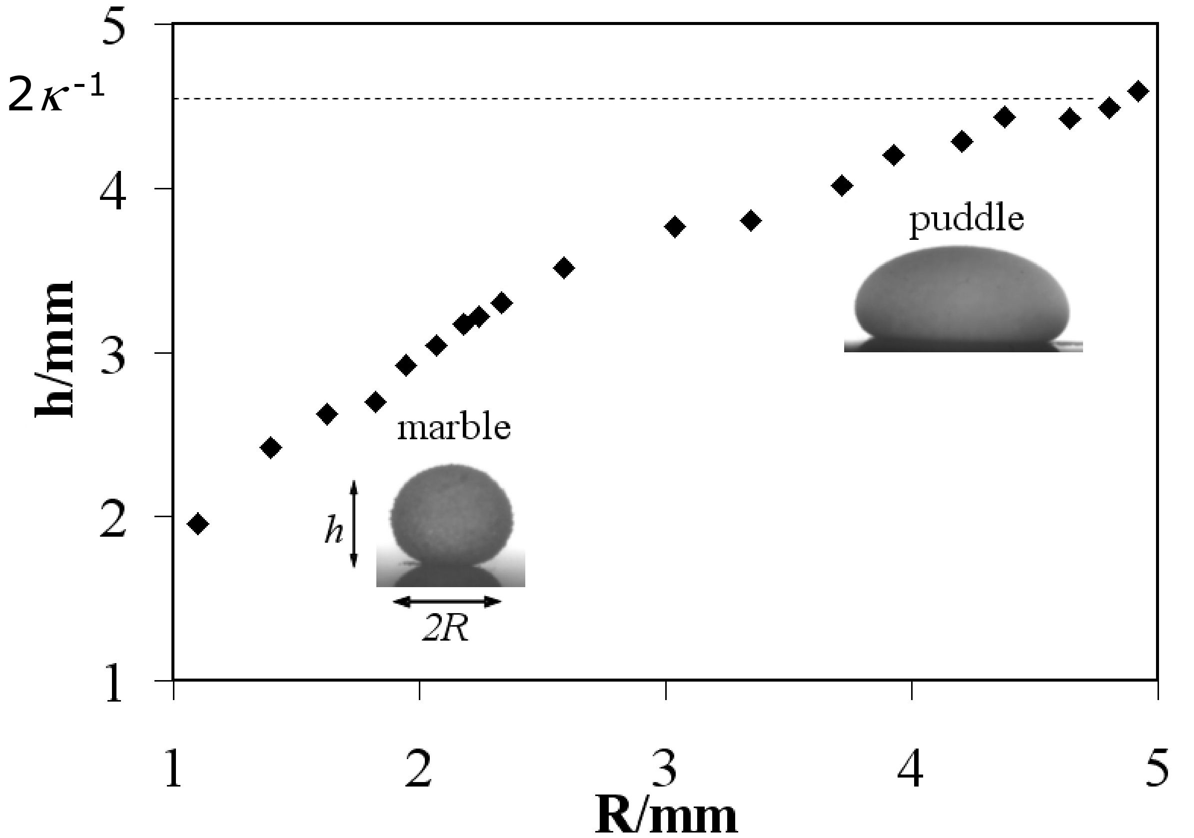
Liquid Marbles – Size Data

Hydrophobic lycopodium plus 0.01M KCl deionised water

Transition from marble to puddle with increasing volume

Limiting value of puddle height gives twice the capillary length, $h=2\kappa^{-1}$



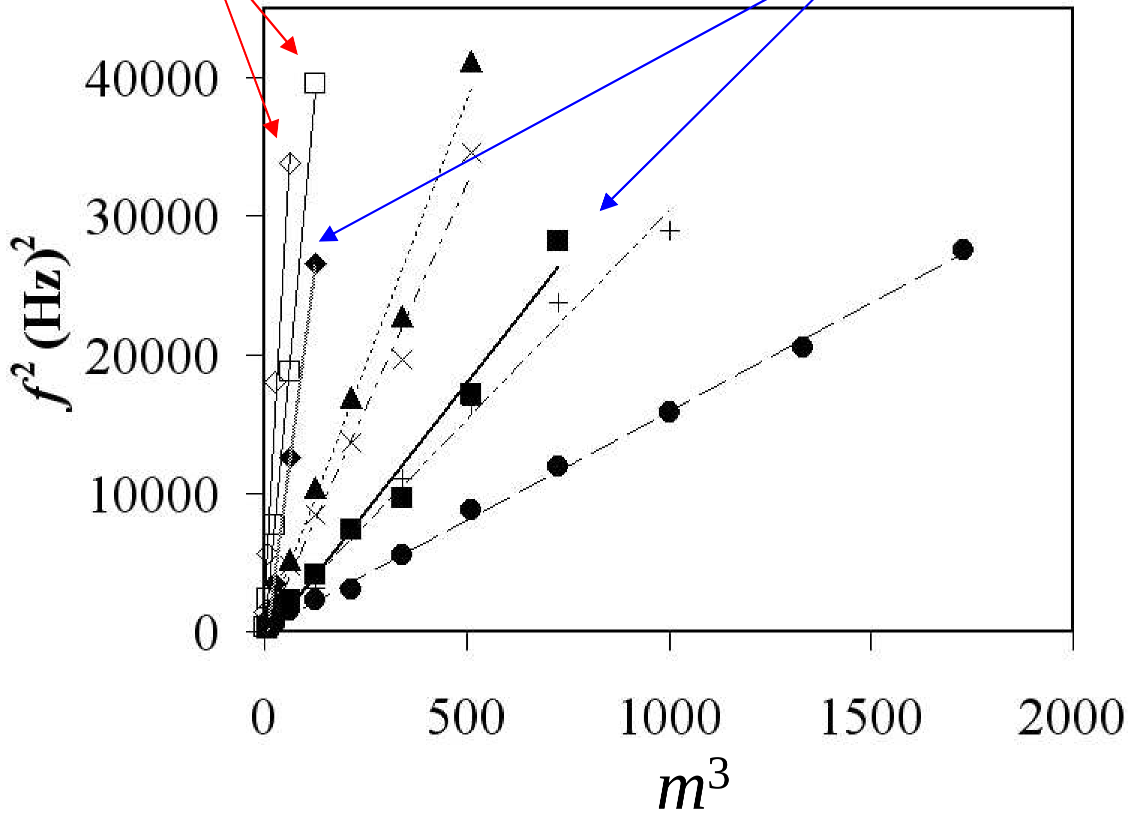
Inset are images taken for marble of radius 1.1 mm and puddle of radius 4.8 mm.

Mode Dependence (Droplets and Marbles – Subject to possible errors in droplet data)

Square of frequency as a function of mode number, *m*, cubed

Droplets of volumes 10 µl (◇) and 100 µl (□)

Liquid marbles of volumes 10 µl (♦) and 100 µl (■)



Other liquid marble volumes shown:

30 µl (▲)

50 µl (x)

125 µl (+)

150 µl (●)

Note: Lines are trend lines and not fits