Introduction to research activities exam

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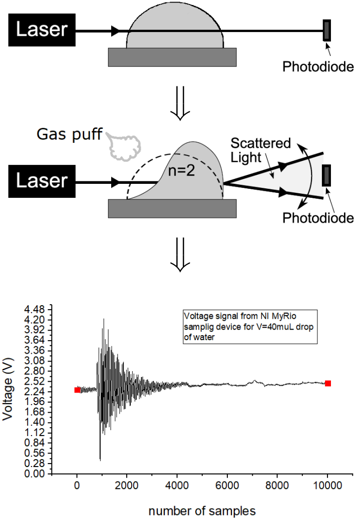
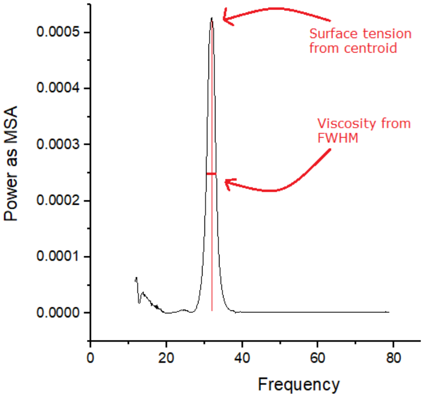
Abstract

Title of the experience:
Rheological measurements of non-newtonian liquids based on drop oscillation.

This research activity deals with the reproduction of a rheometer by means of an implemented *ad hoc* experimental apparatus to study vibrational normal modes of submillimetric sessile drops (volumes of $pL/\mu L$), from which it is possible to estimate **viscosity** and **surface tension**.

Principle of the experiment

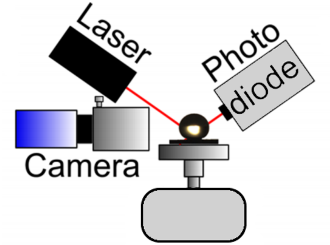




Aim of the experience

- To reproduce a **Rheometer**
- To find the resonance spectra
- To compute surface tension and viscosity
- To repeat the process for **Newtonian** liquids: water and glycerine solutions: 60%,75%,85%.

$\Downarrow$



Basic theory - Viscosity

The viscosity of a fluid is a measure of its resistance to deformation at a given rate.

Shear Rate:

$$\dot{\gamma} = \frac{\partial v}{\partial z}$$

Shear stress:

$$\tau = \frac{F}{S}$$

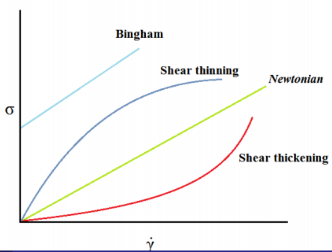
The constant of proportionality between the two rheological quantities is the viscosity coefficient:

Newtonian Fluids:

$$\tau = \eta\dot{\gamma}$$

Non-Newtonian Fluids:

$$\tau = \eta(\dot{\gamma})\dot{\gamma}$$



Basic theory - Surface tension

Surface tension σ is the energy, or work, due to intermolecular forces, required to increase a unit of the surface area.

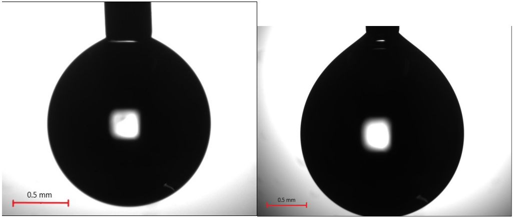
$$\sigma = \left(\frac{\partial G}{\partial A}\right)_{T,p} = \frac{dF}{dL} \tag{1}$$

In **Microfluidics** capillary force dominate over gravity force

Bond Number:

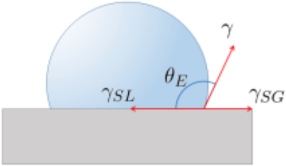
$$Bo = \frac{F_{gravity}}{F_{capillary}} =$$

$$= \frac{\rho g L^2}{\sigma} << 1.$$



The contact angle is the angle between the solid/liquid and the tangent to the liquid/air interface where they meet. It quantifies the wettability of a solid surface by a liquid via the Young equation:

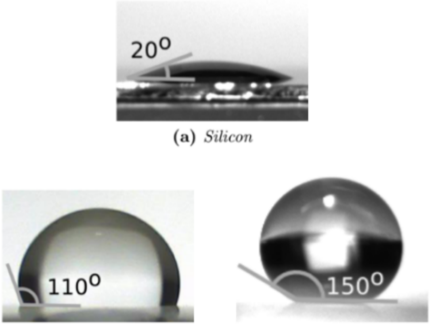
$$cos\theta_E = \frac{\sigma_{SG} - \sigma_{SL}}{\sigma}. \tag{2}$$



wettability

Depending on the contact angle we can define:

- $\theta_E = 0^\circ$ *perfect wettability*;
- $\theta_E < 90^\circ$ *hydrophilic*;
- $\theta_E > 90^\circ$ *hydrophobic*;
- $\theta_E > 150^\circ$ *super hydrophobic*.



(a) *Silicon*

(c) *PDMS*

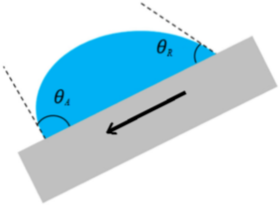
(d) *Superhydrophobic*

Pinning and hysteresis of contact angle

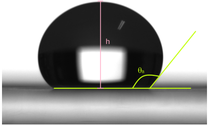
Contact line: three phase separator line.

hysteresis of contact angle: is the result of the activation energy required for movement of a droplet from one metastable state to another on a surface, caused by asperity, impurities or chemical or physical disomogeneity in an interval $\theta = [\theta_R; \theta_A]$ (Reciding A. and Advancing A.).

Pinning:when the contact line remains blocked and the contact angle undergoes a phenomenon of hysteresis.

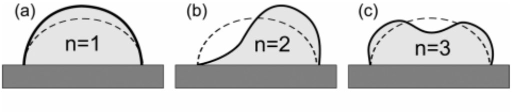


In proposed models, a drop is seen as a **damped oscillator**.
Hipotesis: Pinned contact line, hydrophobic substrate, capillary force predominate over gravity force



- *Sharp et al.* - **2011** Analysis of vertical modes for droplets in capillary regime considering a spherical surface. An homogeneous factor of $\alpha \simeq 0.81$ is found to correct the formula:

$$f_n \simeq \alpha \frac{\pi}{2} \sqrt{\frac{n^3 \sigma}{24 \rho V} \frac{cos^3\theta - 3cos\theta + 2}{\theta^3}} \tag{3}$$



Temperton theory and Viscosity calculus

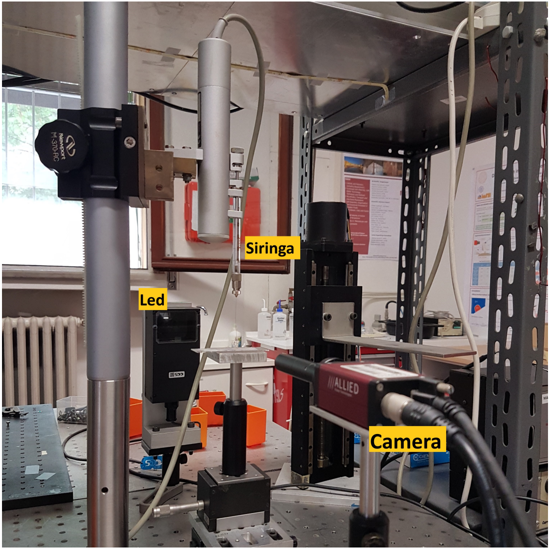
- *Temperton et al.* - **2013** Improved the Sharp's formula by including a geometrical factor that represents the height of the drop:

$$f_n = \frac{1}{\pi 2}\sqrt{\frac{n^3\sigma\pi}{4\rho V} tanh\left[\frac{n\pi}{4\theta}\frac{-cos^4\theta + 6cos^2\theta - 8cos\theta + 3}{cos^3\theta - 3cos\theta + 2}\right]} \qquad (4)$$

Viscosity:
R. Temperton - **2012** The oscillations decay exponentially with time such that the amplitude scales with $e^{-\Gamma t}$ where Γ is the damping coefficient:

$$\Gamma_{bulk} = \frac{2}{\rho}\left(\frac{n\pi}{L}\right)^2 \eta \qquad with\ \Gamma_{bulk} = FWHM \qquad (5)$$

Setup 1



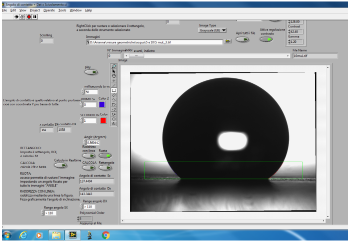
Equipment:

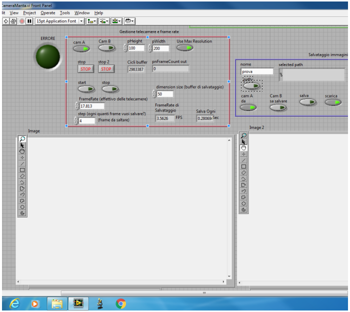
- focused Led
- Teflon/Parafilm
- ALLIED cam + telecentric lens (425 pixel/mm)
- Syringe driver ($\mu L/nL$)
- LabView program to acquire video and angles computation

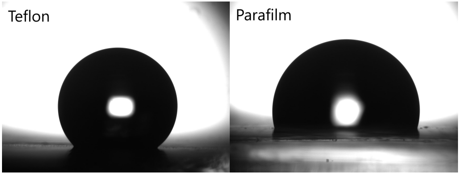
Purposes:

- Characterization of Young angle
- Hysteresis measurements of contact angle to choose the substrate
- Standard study of surface tension with "Pendant Drop" method

LabView analysis







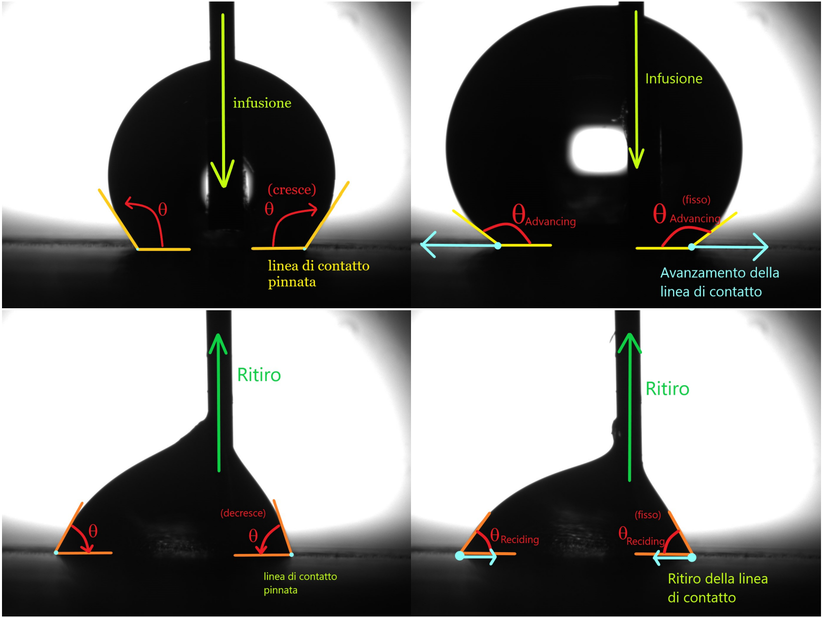
UP water:

	$\theta_{contact}$	$\theta_{reciding}$	$\theta_{advancing}$
Teflon	$125^\circ \pm 4^\circ$	$59^\circ \pm 6^\circ$	$144^\circ \pm 3^\circ$
Parafilm	$100^\circ \pm 4^\circ$	$33^\circ \pm 3^\circ$	$105^\circ \pm 3^\circ$

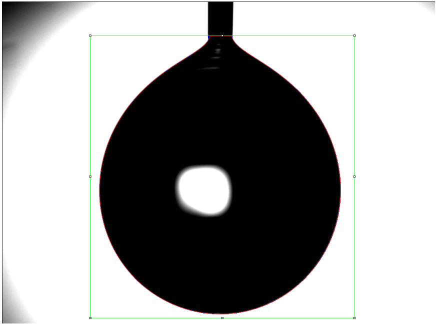
Glycerol + water:

Teflon	$\theta_{contact}$
gly 60%	$127^\circ \pm 7^\circ$
gly 75%	$133^\circ \pm 11^\circ$
gly 85%	$134^\circ \pm 13^\circ$

Captured images for the hysteresis study

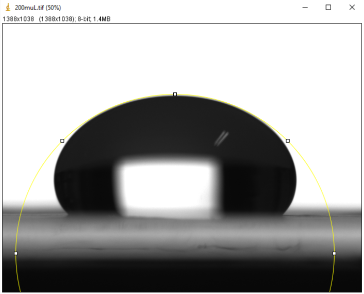


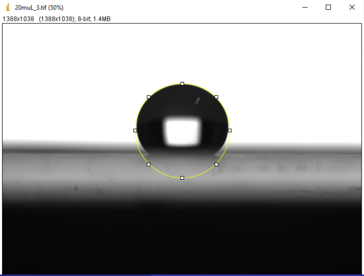
Imeagej analysis:surface tension preliminar study and droplet radius



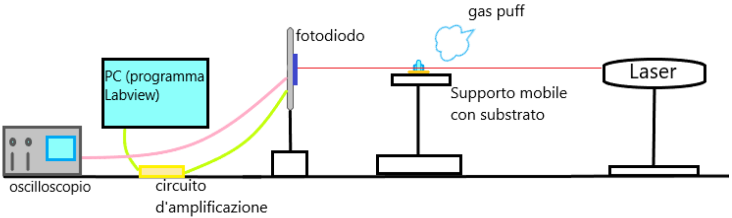
↑Pendent Drop profile generation and fitting

Geometry of drop profile →

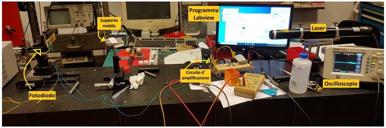


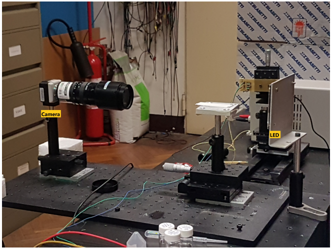


Setup 2

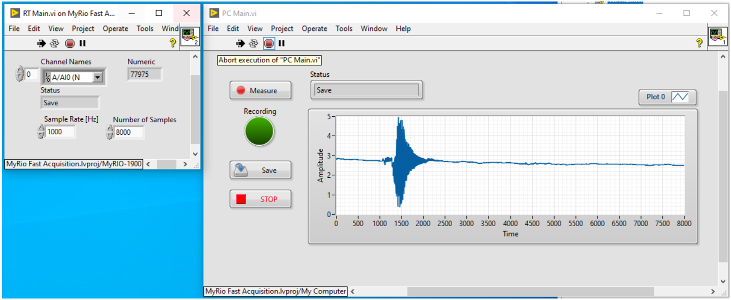


- Laser (IIIB)
- LED
- ALLIED cam with NAVITAR lens
- photodiode
- Oscilloscope
- Amplification circuit
- Data acquisition module (NATIONAL INSTRUMENT MyRio)
- Labview programme





Setup 2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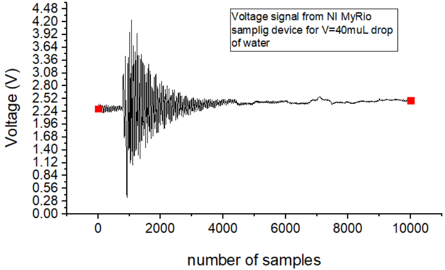
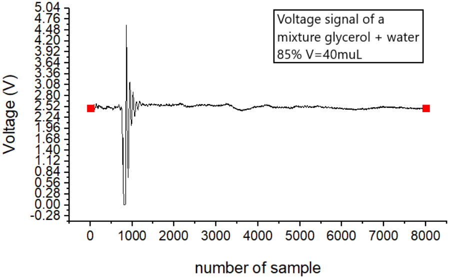
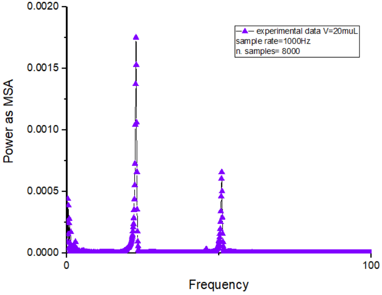
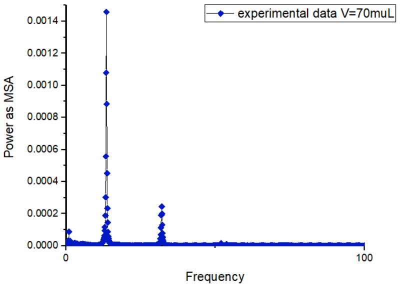
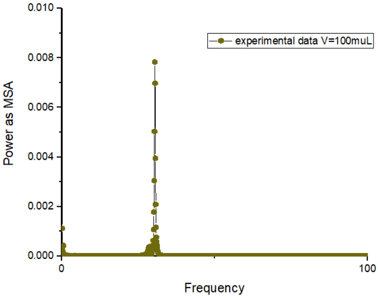

Voltage signal from NI MyRio samplig device for V=40muL drop of water
Voltage (V)
number of samples

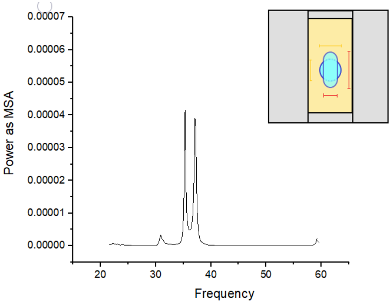

Voltage signal of a mixture glycerol + water 85% V=40muL
Voltage (V)
number of sample

UP water results



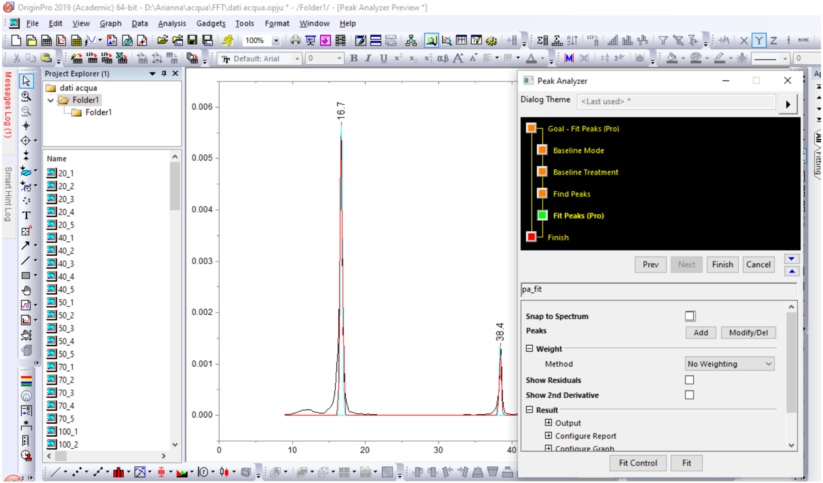






Peak Analizer

Peak Analizer by Origin



UP water results

Frequencies with Sharp's formula (Hz):

	$20\mu L$	$40\mu L$	$50\mu L$	$70\mu L$	$100\mu L$
n=2	$24,5 \pm 0,02$	$17,3 \pm 0,01$	$15,5 \pm 0,01$	$13,09 \pm 0,008$	$10,96 \pm 0,007$

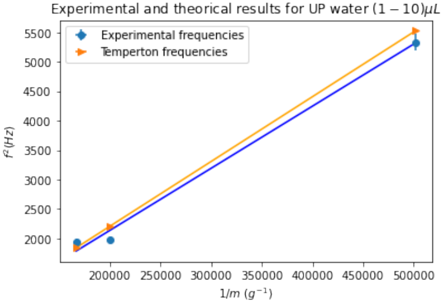
Frequencies with Temperton's formula (Hz):

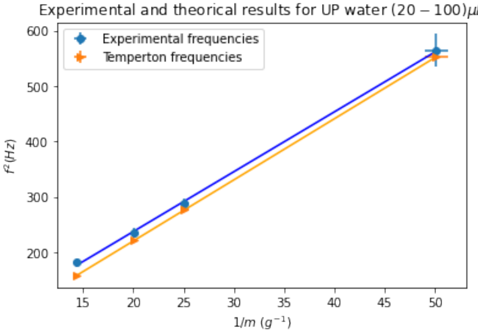
	$20\mu L$	$40\mu L$	$50\mu L$	$70\mu L$	$100\mu L$
n=2	$23,51 \pm 0,01$	$16,624 \pm 0,007$	$14,869 \pm 0,006$	$12,567 \pm 0,004$	$10,514 \pm 0,003$

Experimental resonant frequencies (Hz):

	$20\mu L$	$40\mu L$	$50\mu L$	$70\mu L$	$100\mu L$
n=2	$23,8 \pm 0,6$	$17,0 \pm 0,3$	$15,3 \pm 0,4$	$13,47 \pm 0,9$	

UP water results





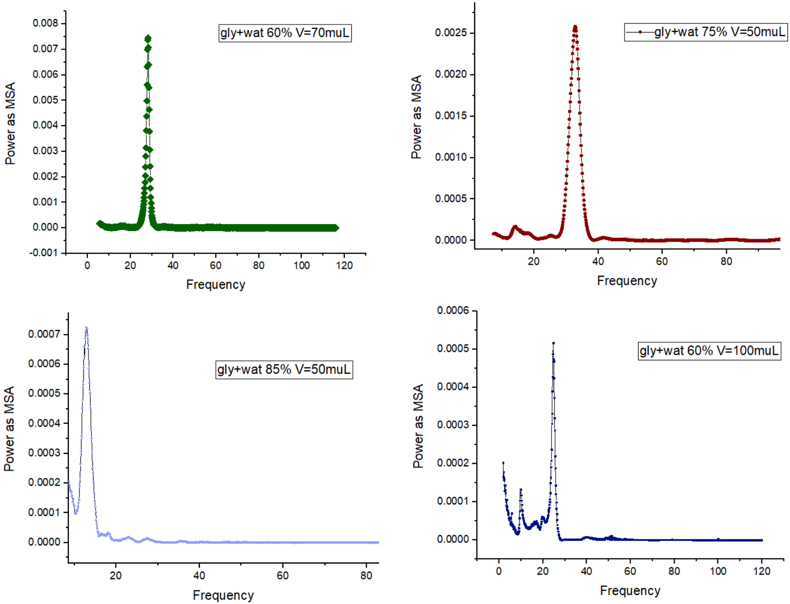
glycerol+water results

gly 60%	$20\mu L$	$40\mu L$	$50\mu L$	$70\mu L$	$100\mu L$
th. (Hz)	$21,13 \pm 0,01$	$14,941 \pm 0,008$	$13,364 \pm 0,007$	$11,295 \pm 0,005$	$9,451 \pm 0,004$
exp (Hz)	$20,2 \pm 0,6$	$14,1 \pm 0,2$	$12,7 \pm 0,8$		

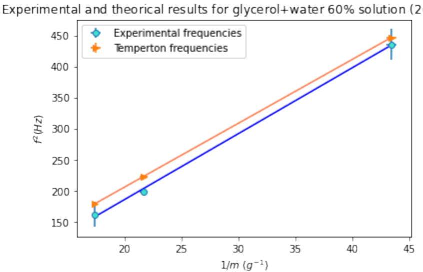
gly 75%	$20\mu L$	$40\mu L$	$50\mu L$	$70\mu L$	$100\mu L$
th. (Hz)	$20,36 \pm 0,01$	$14,396 \pm 0,009$	$12,876 \pm 0,008$	$10,882 \pm 0,007$	$9,105 \pm 0,006$
exp (Hz)	$19,5 \pm 0,6$	$13,99 \pm 0,8$		$11,46 \pm 0,6$	$\simeq 11,1281$

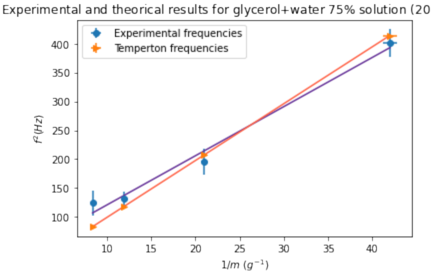
gly 85%	$20\mu L$	$40\mu L$	$50\mu L$	$70\mu L$	$100\mu L$
th. (Hz)	$20,06 \pm 0,01$	$14,191 \pm 0,009$	$12,683 \pm 0,008$	$10,728 \pm 0,007$	$8,975 \pm 0,005$
exp (Hz)	$17,01 \pm 0,7$	$13,43 \pm 0,3$	12 ± 1	$10,9 \pm 0,3$	$\simeq 8,48315$

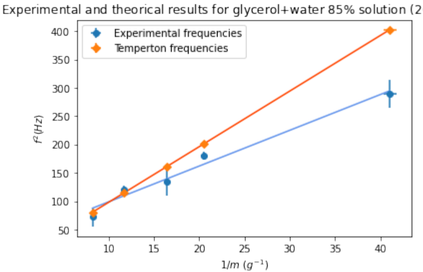
glycerol+water results

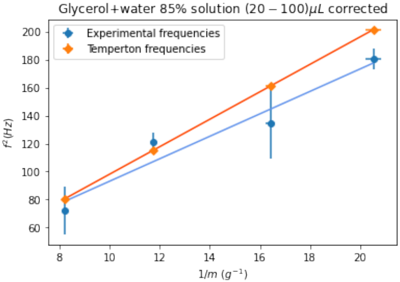


glycerol+water results









Results - *surface tension*

Used formula:

$$\sigma = (2\pi)^2 F_n^2 \frac{4\rho V}{\pi n^2} \frac{1}{tanh\left[\frac{n\pi}{4\theta} \frac{-cos^4\theta + 6cos^2\theta - 8cos\theta + 3}{cos^3\theta - 3cos\theta + 2}\right]} \tag{6}$$

Results:

(mN/m)	Literature*	Experimental (Pendant Drop)	Experimental (using experimental frequencies)
Acqua UP	$\simeq 72$	$72,2 \pm 0,3$	73 ± 1
gly 60%	$\simeq 67$	$66,9 \pm 0,5$	70 ± 2
gly 75%	$\simeq 65$	$64 \pm 0,6$	67 ± 2
gly 85%	$\simeq 63$	63 ± 1	59 ± 3

*da *Physical properties of glycerine and its solutions* - C. S. Miner and N. N. Dalton.

Results - *viscosity*

Used formula:

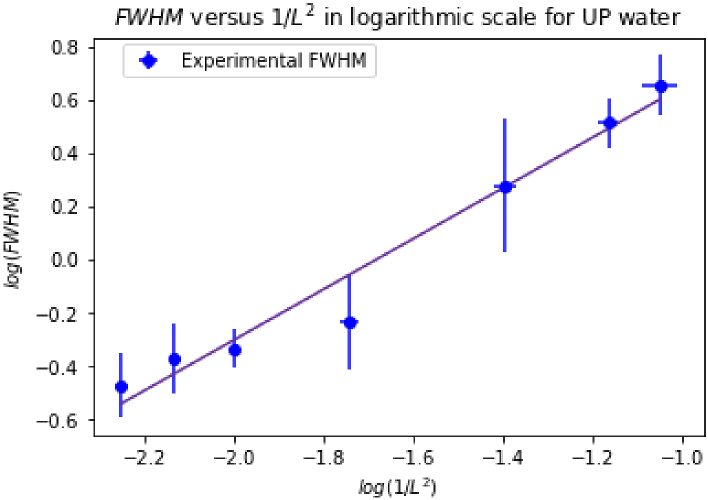
$$\eta = \frac{\Gamma_{bulk}}{\frac{2}{\rho}\left(\frac{n\pi}{L}\right)^2}, \qquad with\ \Gamma_{bulk} = FWHM \tag{7}$$

Results:

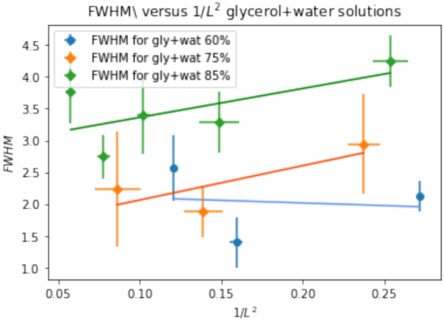
(mPa/s)	Literature* (T=30°)	Experimental
Acqua UP	$\simeq 1$	$1,25 \pm 0,02$
gly 60%	$\simeq 7,19$	$7,3 \pm 0,1$
gly 75%	$\simeq 21,2$	$22,4 \pm 0,4$
gly 85%	$\simeq 58$	$52,6 \pm 0,3$

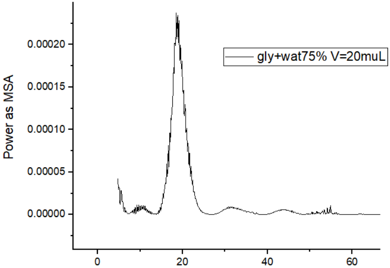
*da *Physical properties of glycerine and its solutions* - C. S. Miner and N. N. Dalton.

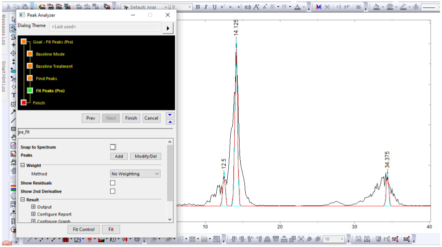
Graphics -Water



Graphics - Glycerol solutions







Conclusions

In this research activity I studied rheological properties of some type of Newtonian fluids.

Problems that I found:

- Uncontrolled gas puff
- Lack of data for some volumes
- Peak shape not always proper for data analyzing

Possible solutions:

- To get a gas diffuser to be controlled remotely by an electrovalve
- Increase the statistics and create better ambiental conditions
- Program a software to control better the fitting parameters and improve the signal

Once the apparatus will be optimized, it will be possible to proceed to analize non-newtonian fluids.