Dynamics of a contact line at the nanoscale

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Abstract: In this TFG we analyze two features of the contact line: the fluctuations around a stationary position and the Contact Angle Hysteresis(CAH). We give an expression for the power spectrum of the fluctuations, and we discuss a model for the CAH. These phenomena have been addressed experimentally, which we will use to show the validity of our model.

I. INTRODUCTION

The dynamics around a contact line(the geometrical place where a solid surface, a liquid and air join) is fundamental in fluid physics, and is also crucial in many industrial processes such as spreading of droplets or entrainment of fluids.

This area of study has a lot of phenomena. Here we are going to focus in two of them: the fluctuations of the contact line around a stationary position and the Contact Angle Hysteresis(CAH) . Using AFM (Atomic Force Microscopy) with a cantilever glued onto a glass fibre (Fig 1)), you can easily see these features, and analyze them experimentally. Some experiments[1], [2], [3] have been done about it, but we still are not having a complete theoretical comprehension of it. In this report we will give a theoretical explanation of the hysteresis loop and the power spectrum of those fluctuations.

We can see the fluctuations of the contact line around a stationary position when the tip of the glass fibre touches the fluid-air interface of a fluid at rest. When this happens, the contact line will form, and the contact line, which will be pinned to the glass fibre, will begin to oscillate, because of the random thermal impulses. It is used in [1] to measure the friction coefficient of the contact line. We will analyse those fluctuations, giving an expression for the spectral distribution of those random oscillations.

Discussing about the Contact Angle Hysteresis implies discussing about the contact angle. The contact angle is intrinsically related to the contact line, because its the angle under which the liquid wets the solid surface(inset of Fig.1 a)). Keeping this in mind, if you pull a circular contact line downward a certain distance, then you stop, and you pull it upward again within the glass fibre of a cantilever at a constant speed u, and you measure the contact angle θ in function of time t or traveling distance $s = ut$, you will find a hysteresis loop. In [2] is presented an experiment which shows the existence of this hysteresis loop at the nanoscales, using this experimental setup. The existence of the CAH is due to the fact that the contact angle is different in the advancing(downward) and in the receding(upward) movement. In fact, the cantilever is measuring the capillary force acting on the contact line

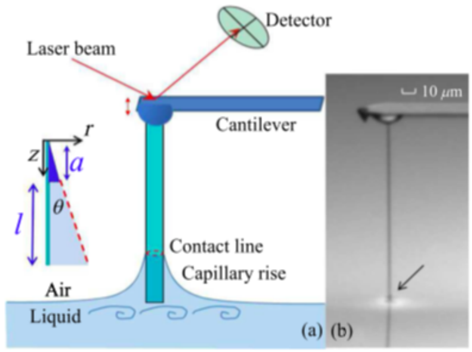

FIG. 1: (a) Sketch of the AFM experimental setup and the capillary rise around the glass fibre. Inset shows the contact angle and the coordinate system we will use. (b) Glass fibre used in the experiments, of $d = 2.2\mu m$. The arrow points to the contact line. Photo courtesy of P.Tong in [1]

$$f = -\pi d\gamma \cos\theta \quad (1)$$

, where d is the diameter of the glass fibre and γ the surface tension of the liquid. The minus sign is defined as $f \leq 0$ for $\theta \leq 90^o$

In the report we present an example of such a hysteresis loop, from an experiment[2], for a certain fluid at a certain speed u, and we will give a model consistent with the experiment of the loop. In this experiment, they measure the hysteresis loop for different fluids and travel speeds in order to show the dependence of the loop with these parameters. Understanding these two effects is useful for a lot of applications. For example, if we understand the spectrum amplitude of the fluctuations around a stationary position, we will correct the measures involving AFM, because we will have this error source controlled.

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II. FLUCTUATIONS OF THE CONTACT LINE

We need some previous definitions:
Let $z(t)$ be a function of time. We define its Fourier Transform (FT) as

$$Z(\omega) := \int_{-\infty}^{\infty} e^{-i\omega t} z(t)\, dt$$

We will use capital letters (or FT) to define the Fourier Transform of a function. Let now $z(t)$ be a stochastic function of time. We define $\langle z(t)\rangle$ as the arithmetical mean of z for all the noise realizations at a time t, and we note it is a function of time
We also define

$$\langle Z(w)\rangle := FT\langle z(t)\rangle$$

This definition only makes sense for strictly stochastic functions. Finally we define the power spectrum of $z(t)$ as

$$\left\langle |Z(\omega)|^2 \right\rangle$$

We also need to introduce the Wiener-Kinchin Theorem, whichs says that

$$\left\langle |Z(\omega)|^2 \right\rangle = FT\langle z(t)z(0)\rangle$$

The right part of the equality is called the correlation function.
Our system can be modelled by the following stochastic differential equation:

$$\frac{d^2z}{dt^2} + \frac{\xi}{m}\frac{dz}{dt} + \omega_0^2 z = \frac{1}{m} f_{Th}(t) \tag{2}$$

Here z is the position of the contact line (or the cantilever position, because there is pinning), m is the mass of the cantilever, ξ is the friction coefficient of the contact line , and $\kappa_0 = \omega_0^2 m$, where κ_0 is the elastic constant of the system. As we have said, our ODE (Ordinary Differential Equation) is stochastic, because $f_{Th}(t)$ is a white noise function due to the thermal fluctuations of the fluid in contact with the cantilever, which is continuous. So, at every time instant t we will have some noise realizations, with

$$\langle f_{Th}(t)\rangle = 0 \tag{3}$$

$$\langle f(t)_{Th} f_{Th}(t')\rangle = 2\xi\kappa_B T\delta(t-t') \tag{4}$$

In these expressions κ_B is Boltzmann constant, T is the temperature of the fluid and δ is Dirac Delta Function.
We will apply FT to this ODE, using its linearity:

$$-\omega^2 Z(\omega) + \frac{\xi}{m} i\omega Z(\omega) + \omega_0^2 Z(\omega) = \frac{1}{m} F(\omega)$$

This is a standard lineal algebraic equation that we can easily solve,

$$Z(\omega) = \frac{\frac{1}{m}F(\omega)}{(\omega_0^2 - \omega^2) + i\frac{\xi}{m}\omega}$$

and taking the square of the modulus (using the mathematical complex variable property which says that the product of modulus is the modulus of the product) we get:

$$|Z(\omega)|^2 = \frac{\frac{1}{m^2}|F(\omega)^2|}{(\omega_0^2 - \omega^2)^2 + \frac{\xi^2}{m^2}\omega^2}$$

Finally, and as our objective is to find the power spectrum of $z(t)$, we can do the next step:

$$\left\langle |Z(\omega)|^2 \right\rangle = \left\langle \frac{\frac{1}{m^2}|F(\omega)^2|}{(\omega_0^2 - \omega^2)^2 + \frac{\xi^2}{m^2}\omega^2} \right\rangle =$$

$$= \frac{\frac{1}{m^2}\left\langle |F(\omega)^2| \right\rangle}{(\omega_0^2 - \omega^2)^2 + \frac{\xi^2}{m^2}\omega^2}$$

The second equality is justified because, as we commented at the beginning, $\langle\rangle$ only makes sense for stochastic variables. On the other hand, thanks to Wiener-Kinchin Theorem, we know

$$\left\langle |F(\omega)|^2 \right\rangle = FT\langle f(t)f(0)\rangle = 2\xi\kappa_B T \tag{5}$$

Here, we are using that $FT\delta(t) = 1$ In order to end this discussion, introducing the last result in the expression for $\langle |Z(\omega)|^2\rangle$ we get our final result:

$$\left\langle |Z(\omega)|^2 \right\rangle = \frac{2\kappa_B T\xi}{m^2\left[(\omega_0^2 - \omega^2)^2 + \frac{\xi^2}{m^2}\omega^2\right]} \tag{6}$$

We can see that the fluctuations of the contact line around a stationary position have a dependence with ξ, so it can be used to get a measure of the friction coefficient, as we commented in the Introduction. We also see that there is a predominant frequency which is ω_0, because maximizes (6). This means that if you represent $z(t)$, the plot will have noise peaks repeated with that frequency.

III. THE HYSTERESIS LOOP

First of all, we present the experimental loop we have talked about in the Introduction, in order to work in the parts we are going to focus on.

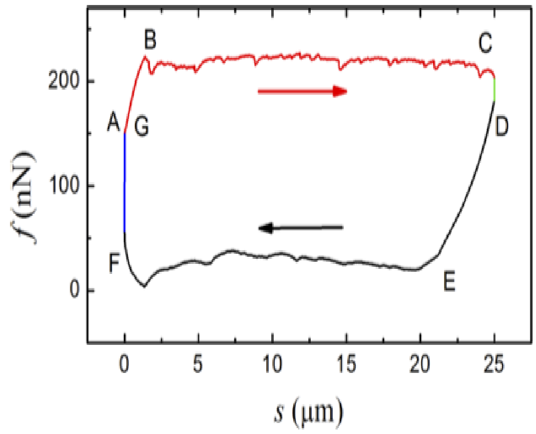

FIG. 2: Hysteresis loop for water, with speed $u = 10\mu m/s$. The magnitudes measured are s (the travelling distance of the cantilever) and f (the capillary force).→ means downward and ← means upward. Photo courtesy of P.Tong in [2]

In this loop we see 3 different parts of the hysteresis cycle. The first one is a linear part, from an initial static angle θ_0 to a final angle θ_i where $i = u$(upward) or $i = d$(downward). The second one is pinning-depinning fluctuations part, with the contact angle fluctuating around θ_i and the third one is a relaxation part in which the cantilever is not moving and the contact angle relaxes. This is the essence of what there is behind this particular phenomenon.

There are other interesting effects, such as the asymmetry of the loop, or the dependence of it with u. We will give a complete model for the linear part and we will give an equation to determine the depinning point; this is, the point where we change from the linear part to the horizontal part. Also, we will make a proposal for the pinning-depinning fluctuations

In order to relate this picture with the Introduction, A-B and D-E are the linear parts, B-C and E-F are the horizontal parts and C-D and F-A are the relaxation parts

A. Linear part. A to B(advancing) or D to E(receeding)

Here we are interested to show the linear part of the CAH, where the contact line is pinned and pulling upward or downward the cantilever produces a linear variation of contact line with the distance travelled. First of all, we will find an expression for the meniscus shape in this situation. De Gennes[4] provides for us an equation for this. We will work in cylindrical coordinates due to the geometry of our problem(See inset of Fig.1). If r is the radial coordinate and z is the height coordinate(its zero is at the height in which the fluid is plain($\theta = 0$)), the equation is

$$\frac{r}{\sqrt{1+\left(\frac{dr}{dz}\right)^2}} = b \qquad (7)$$

where $b = \frac{d}{2}\cos\theta_0$, being θ_0 the equilibrium contact angle(this is, the angle under which the fluid wets the solid surface in equilibrium, in point A or D, without pulling upward or downward. The physical meaning of the equation is imposing that the forces acting on a portion of the fluid(capillary force and the force exerted by the glass fibre) must add up to 0. If you solve this equation, you get

$$r(z) = b\cosh\left(\frac{z-h}{b}\right) \qquad (8)$$

In order to find the integration constant h, we need to impose a physical boundary condition: r cannot tend to infinite, so we assume that $r(z=0) = l$, where $l = \sqrt{\frac{\gamma}{\rho g}}$ is the capillary length. For distances less than l, gravity can be neglected(assumption which is implicit in the differential equation), making our model consistent with the assumptions. So, we get

$$h = b\ln\frac{2l}{b}$$

Now we are about to find a relation between the meniscus height H and the dynamical angle θ. This can be obtained from the $r(h)$ profile, because $\frac{d}{2} = r(z = H)$. With this, we obtain

$$H = \frac{d\cos\theta_0}{2}\ln\left(\frac{4l}{d(1+\sin\theta_0)}\right)$$

We are now close to our final result (the spring constant of the capillary force). In order to do this, we need to compute $\frac{dH}{d\theta_0}$:

$$\frac{dH}{d\theta_0} = -\frac{d}{2}\left[1-\sin\theta_0\left[1+\ln\left(\frac{d}{4l}(1+\sin\theta_0)\right)\right]\right]$$

With this, it is easy to see that

$$\frac{d(\cos\theta_0)}{dH} = -\sin\theta_0\frac{1}{\frac{dH}{d\theta_0}} =$$

$$= \frac{2\sin\theta_0}{d\left[1-\sin\theta_0\left[1+\ln\left(\frac{d}{4l}\left(1+\sin\theta_0\right)\right)\right]\right]}$$

In point A of the CAH, we have $f = -\pi\gamma d\cos\theta_0$, and we are at equilibrium. If we pull upward the cantilever a small distance δH, at the new equilibrium, the contact angle will have changed from θ_0 to $\theta_0+\delta\theta_0$ because the CL will be stretched. This phenomena produces a change in capillary force, which is translated into a restoring force, and its spring constant can be computed as the derivative of f respect H. This is:

$$\kappa = \pi\gamma\frac{d(\cos\theta_0)}{dH} =$$

$$= \frac{2\pi\gamma\sin\theta_0}{1-\sin\theta_0\left[1+\ln\left(\frac{d}{4l}\left(1+\sin\theta_0\right)\right)\right]} \tag{9}$$

As we can see, we have made this computation for small changes in θ_0, and supposing that when these changes are made at low u, to have equilibrium states in all the way. So, we expect that when the change in θ_0 is big enough, the corresponding profile in CAH is not linear anymore.
This fact can be seen in Fig.2. In the receding direction, there is a big change in the angle before the depinning, and for the lower angles (lower f) there is no lineal profile. We also notice that this expression does not depends on the advancing or receding direction, only if the angle change is big or small, so it can explain both A-B and D-E parts of the hysteresis loop in Fig.2, if the angle has a small change.
We present now a graphic with the experimental measurements of κ [3],[2] and their fit to (9):

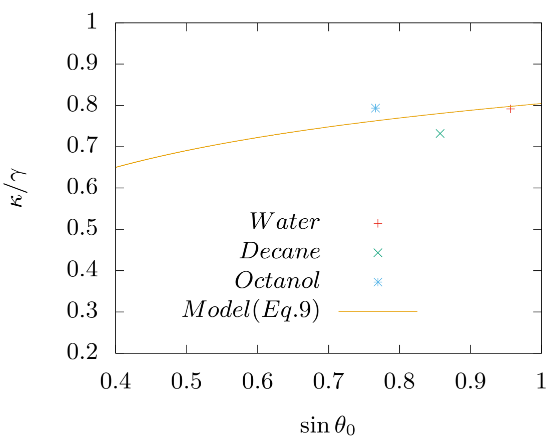

FIG. 3: Plot of the model(Eq.9) and three experimental results for κ[3]. These are for water, decane and octanol. The model is computed assuming $d = 2.2\mu m$

B. Depinning point. B or E

As we have said before, in the linear part, the contact line is pinned to the cantilever. At a certain point (B or E in Fig.2) there is a depinning of the contact line. At this point, the restoring force of κ coefficient gets equal to the capillary force difference

$$\Delta f = \pi d\gamma|\cos\theta_0 - \cos\theta_d| \tag{10}$$

We work with the module. Thanks to this, the equation gets independent of whether the cantilever goes upward or downward. If we equalise this force difference to the restoring force, we get an expression which allows us to find the depinning point:

$$\kappa s = \pi d\gamma|\cos\theta_0 - \cos\theta_d| \tag{11}$$

Remember that s is the traveling distance of the cantilever, this is, the depth at which the glass fibre is. To prove the validity of this equation, we present a table where we calculate the relative difference (Relat. Diff.) between the two terms of (11) for the experimental data(from reasonable values of Fig.6 in [2]) of the same liquids in Fig.3. It must be close to 0. The relative difference have been computed with

$$\frac{|\kappa s - \pi d\gamma|\cos\theta_0 - \cos\theta_d||}{\kappa s} \tag{12}$$

Fluid	$\theta_d(^o)$	$\theta_0(^o)$	$s(\mu m)$	Relat. Diff
Water	120	107	1.9	0.04
Decane	69	59	1.3	0.01
Octanol	65	50	2	0.05

TABLE I: Table which shows the validity of Eq.11.We have done the calculations with the κ coefficients computed in the previous section.

As we can see, we can conclude that our simple equation is valid, because the relative difference between its two terms is very close to 0.

C. Pinning-depinning fluctuations. B-C(advancing) and E-F(Receeding)

We are going to propose a model for this part, using Section II. At point B(or E), the contact line will depin, and it will begin a stick-and-slip motion. This is because the contact line will randomly pin to the glass fibre, and depin because of the motion of the fibre. The contact line will be pinned to the glass fibre and because of that we will have the harmonic oscillator equation. In addition, we will have a random force f_g caused by the defects of the glass fibre, which will randomly depin the contact line. We see that we can modelize this part with an equation similar to (2). Our equation will be (same notation than in Sec. II):

$$\frac{d^2z}{dt^2} + \frac{\xi}{m}\frac{dz}{dt} + \omega_0^2 z = \frac{1}{m}f_g(t) \tag{13}$$

With f_g accomplishing:

$$\langle f_g(t)\rangle = 0$$

$$\langle f(s)_g f_g(s')\rangle = 2D\delta(s-s') = \frac{2D}{u}\delta(t-t')$$

D is a parameter related to the random force. Here we see that thanks to the constant speed motion of the cantilever, i.e, the relation $s = ut$, we have transformed a random spacial depending force, which has a very difficult treatment, to a brownian-like force depending on time, so we can recycle our expression of the fluctuations of Section II, and we obtain:

$$\left\langle |Z(\omega)|^2 \right\rangle = \frac{2D}{um^2\left[(\omega_0^2-\omega^2)^2 + \frac{\xi^2}{m^2}\omega^2\right]} \tag{14}$$

As we commented in the Introduction, we have the fluctuations depending on the velocity of the cantilever. This is very important, because in [2], the hysteresis is speed-depending in these pinning-depinning fluctuations, with lower peaks as u increases, so this could be a reasonable model to explain this part of the hysteresis loop. We also see that there is again a predominant frequency, and we can relate this with the repetition of those peaks in Fig.2.

IV. CONCLUSIONS

The study of a contact line is full of phenomena, such as the two we have studied in this report. By one hand, we have analysed the fluctuations around a stationary value. We conclude that this problem can be modelled like a harmonic oscillator with a brownian random force acting on it. This produces a random oscillation with a predominant frequency, due to the thermal fluctuations. This model can be used to measure the friction coefficient and it can be recycled to explain the fluctuations of the second phenomenon (the hysteresis loop).

On the other hand, we have studied the hysteresis of the contact angle. We have explained completely the first part (the linear one) of the hysteresis loop, modeling it with the existence of a restoring force, which is the capillary force, when the contact line is pinned. We have given an expression of the corresponding elastic constant κ, and we conclude it depends on the contact angle, the geometry and γ. We have a plot in which the experimental data fit our model.

We have given an equation for the depinning point, modeling it as the point where the difference of the capillary force between the equilibrium position and the actual position equals to the elastic force, and we present a table which shows the validity of this equation.

We have proposed a model which explains the pinning-depinning fluctuations of the hysteresis loop, using the results of Section II and modeling the random force which causes the fluctuations like a static random force because of the defects of the glass fibre. With this, we have obtained an expression for the power spectrum of the fluctuations, which is reasonable because shows dependence on u, being consistent with Fig.2. This introduces a question, and it is the value of the dissipation constant D of the static noise. In order to determine its value, we would need to make a numerical simulation of a stochastic differential equation, which it is away of the purposes of this bachelor thesis.

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