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Drawing a single nanofibre over hundreds of microns

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Abstract. – We demonstrate that the limits of drawing of fibre can be pushed down to nanometre dimensions. By a process similar to dry-spinning, nanofibres can be drawn with ultimate dimensions comparable with the ones of single-wall carbon nanotubes. An important difference with tubes is that our nanofibres are produced one at a time. It is also shown that the nanofibre can be positionned precisely on a surface during fabrication, and can then be cut or manipulated by an AFM tip.

Long free-standing fibres and wires of section down to 1 mm are usually fabricated one by one by pulling or extruding them [1]. Below 1 μm , they are better mass fabricated [2] and then separated by dissolving the mould [3] or diluting the original product [4]. But these separation techniques never result in just one fibre at hand. Single metallic nanowires have been fabricated by retracting the tip of a scanning tunnelling microscope (STM) after contact with a surface [5]. Such wires are nanoscale both in section and length, however. In this letter, we report the one-by-one fabrication of very long single fibres, made with citrate molecules, with a section down to a few nanometres. Each fibre is pulled out from a microdroplet or from a micropipette, during the solvent evaporation, just at the threshold of solidification. These fibres extend over hundreds of microns, can be curved through 90° in 10 nm, and be cut and manipulated by an atomic force microscope (AFM) tip.

Drawing a fibre requires a material with a pronounced viscoelastic behaviour to undergo strong deformations, while being cohesive enough to support the stresses developed during the pulling (fig. 1). Furthermore, the pulling process is always accompanied by a solidification that transforms the spinning material into a solid fibre. In the case of melt spinning, this is obtained by cooling, and in the case of dry spinning, by evaporation of the solvent. These

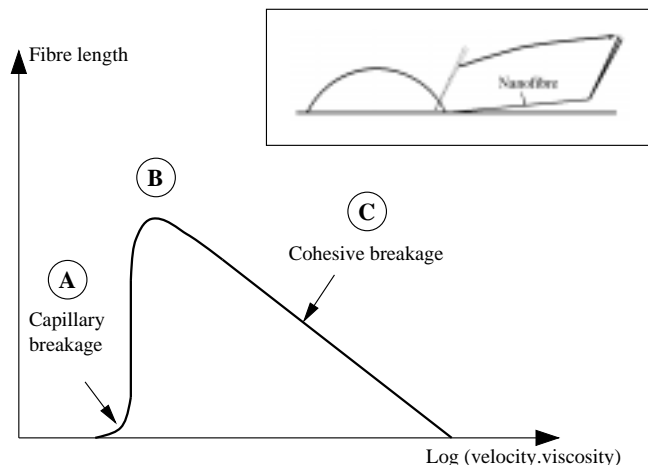


Fig. 1. – Schematic representation of the maximal length of a fibre as a function of the product of the drawing velocity by the viscosity of the source material. The physical mechanisms that determine the breakage of the fibre are of two types: i) the first, important at low viscosity, is associated with surface tension and corresponds to the Rayleigh instability of a liquid jet (phase A); ii) for elastic materials, the deformation energy is stored and, on reaching some limiting value characteristic of the cohesion of the material, results in cohesive, brittle fracture (phase C). In the intermediate phase B long fibres can be pulled as schematised in the inset. In this geometry, the accumulation of material close to the contact line modifies the viscosity and allow to test, on a same droplet, the different regimes discussed above.

complex processes make the final section of the fibre very dependent on the drawing rate, the cooling or evaporation rate and on the precise composition of the material. So far, the standard drawing processes have never produced a fibre with section below $0.2\ \mu\text{m}$ because no material has been found to give, at the maximum of phase B (fig. 1), thinner fibres. For example, it is easy to pull fibres out of a liquid glue just before its solidification [6], but we could not obtain fibres with a diameter below one micrometre. To reduce the diameter of a pulled fibre still further, we have explored the case of solution made of short molecules instead of long polymer chains. In the absence of entanglements, smaller quantities of material will be extracted from the source resulting in much smaller fibres. We pulled the fibres at the threshold of the solidification resulting from evaporation of the solvent at room temperature. The evaporation modifies the properties of the source material allowing to select the optimal viscosity to draw the fibre (phase B in fig. 1).

A freshly prepared aqueous solution of 50 ml of chloroauric acid (0.01% w/v) was boiled under reflux. We added 1.75 ml of an aqueous solution of sodium citrate (1% w/v). The solution turned grey and red in a few minutes due to the fact that this preparation corresponds to the classical Frens method of fabrication of a dispersion of colloidal gold particles [7]. In our case, the mean diameter of the particles, determined by TEM, was 15 nm. These clusters are covered by citrate molecules that are in large excess in the solution [8].

When a millimetric droplet of this solution was deposited on a SiO_2 surface, it evaporated slowly. After a few minutes, the solution became more concentrated at the edge of the droplet due to capillary flow [9]. This appeared as a red coloration close to the contact line. With a micromanipulator, we dipped the extremity of a micropipette with a diameter of one to a few microns close to the contact line. When the solution had suitable concentration, the pipette was withdrawn from the liquid and moved away rapidly (about $100\ \mu\text{m/s}$). The pipette

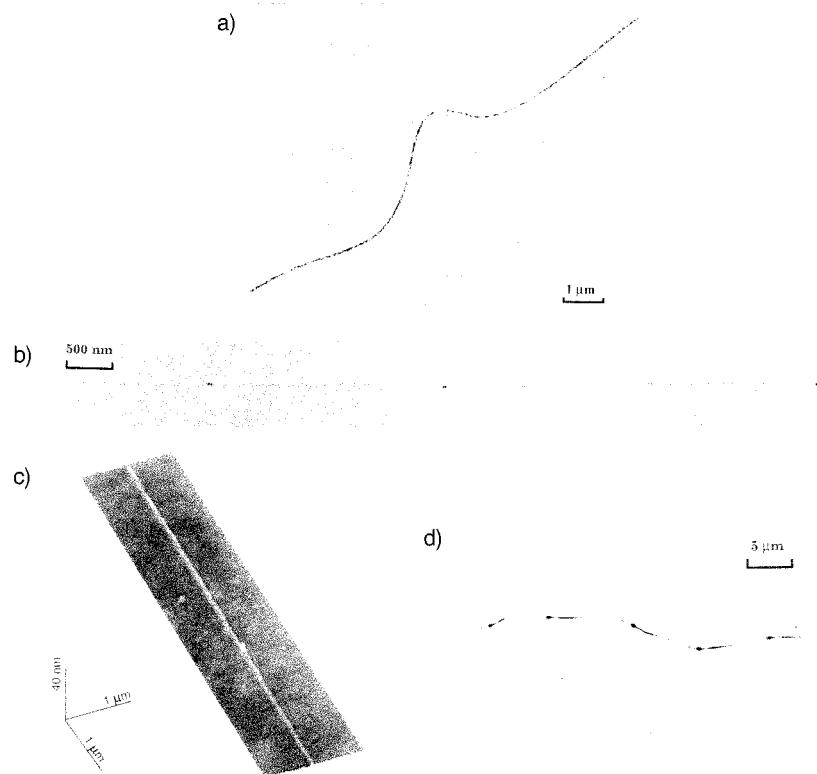


Fig. 2. – Images of different types of fibre obtained: a) TEM image of a part of a millimetre-long fibre with a diameter $\sigma = 60$ nm. b) TEM image of a $100\ \mu\text{m}$ long fibre with a diameter $\sigma = 20$ nm. Only a few gold clusters are embedded in the fibre. c) AFM (Dimension 3000, Digital Instruments) image of a nanofibre obtained in tapping mode. The diameter of the fibre determined as its height is $\sigma = 2$ nm. d) TEM image of a fibre showing a drawing instability. This is always observed with large fibres. The shape is different from the classical Rayleigh instability [10] and is probably due to the presence of the gold clusters.

pulled a fibre that attained in some cases a length of one millimetre. In some cases, the fibre was visible with an optical microscope but in other cases it became rapidly invisible. We could establish the presence of a link between the droplet and the micropipette since a lateral displacement of the micropipette induced a movement of the visible part of the fibre close to the droplet edge. The pulled fibre was deposited by touching the surface with the extremity of the micropipette. We also produced free-standing fibres by drawing from a pipette of larger diameter containing the solution and playing the role of reservoir. The evaporation led to a concentration of the solution at the extremity of the reservoir pipette and a fibre was pulled from this region. This method allowed the deposition of fibres on a surface without wetting it with a droplet.

Transmission electron microscope (TEM) and atomic force microscope (AFM) images of the fibres are shown in fig. 2. From a given droplet, we can pull fibres covering a very large range of sections and lengths. The longest fibres, millimetric in length, have a diameter σ of about $100\ \text{nm}$ (fig. 2a)). In most cases, it is of the order of $20\ \text{nm}$ (fig. 2b)). This is about the size of the gold clusters. In that case, only a few particles are embedded along the fibre.

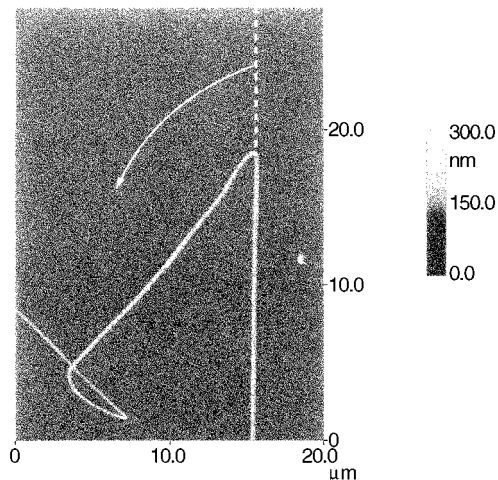


Fig. 3. – Manipulation of a $d = 80$ nm fibre with the micropipette. Before the operation the fibre was straight as shown schematically by the dashed line. The extremity of the fibre was picked up and repositioned making a loop. Note that the fibre is extremely flexible. The corrugation from black to white is 300 nm.

A remarkable point is that we also obtained fibres with section down to 2 nm (fig. 2c)). The length of these nanofibres was about 10 μm . Thus, the simple procedure presented above gives extremely thin fibres with ultimate dimensions comparable with single-wall nanotubes [2]. We observed that the section σ of a fibre is constant over a large part of its length L [11]. Notice that the ratio L/σ stabilised around 10^4 whatever the fibre section is. We also observed, for large fibres obtained just before the cohesive breakage region, signatures of an instability along the fibre (fig. 2d)) as observed during the pulling of fibres with a section in the micron range [10].

The pulling procedure is repeatable several times on every droplet. As the viscosity of the material close to the contact line increases with time, this allows to test the proposed drawing mechanism and to select the viscosity suitable for optimal drawing conditions. At the beginning of the evaporation, the solution at the edge of the droplet was still fluid and the liquid bridge broke by capillary Rayleigh instability corresponding to the part A of the curve of fig. 1. We then observed a sharp transition to a regime where pulling was possible and gave the range of long fibres presented above corresponding to the phase B of fig. 1. It is observed that the diameter of the fibres increased with time: the thinner ones were obtained close to the transition. In the last stage of the droplet evaporation, the solution was very concentrated at the contact line: it was not fluid enough to undergo large deformations and broke cohesively (phase C of fig. 1). Solidification plays an important role during the pulling: if the pulling was stopped for a few seconds, the fibre solidified by solvent evaporation and broke immediately if pulled again. We also verified that the solidification of the fibre did not involve irreversible chemical reticulation by dissolving the fibre locally by passing a water microdroplet through it. The very large flexibility of the fibres indicates that they are not crystallised after solidification. The pulling process described above is therefore similar to the so-called dry spinning of fibres but now extended to molecular scale. We attribute the exceptional length and small diameter of the fibres obtained to the use of small weakly interacting molecules instead of long polymer chains. Such interactions between molecules can also give rise to supramolecular structures in solution as is the case with amphiphiles molecules [12].

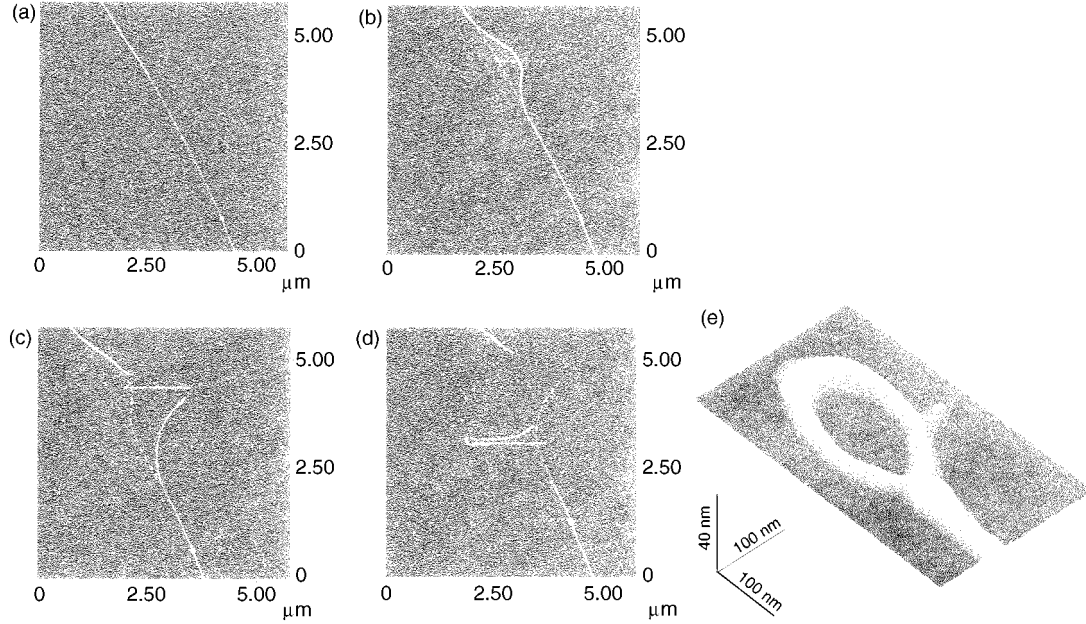


Fig. 4. – Manipulation of a nanofibre with the AFM. The fibre is locally deformed by pushing it with the AFM tip while keeping the feedback loop open. Note that this is possible only when the underneath surface is treated beforehand by chemical grafting of fluorinated chains [13] to decrease the adhesion of the fibre to the surface. a) Image of the $d = 5$ nm fibre as positioned during drawing. The corrugation from black to white is 20 nm. b) A small pushing with the AFM tip (schematised by the arrow) induced a local deformation of the fibre. c) When this pushing is extended the fibre is cut. d) Another manipulation of the fibre leads to the shaping and repositioning of a small hairpin-like open loop. e) A closed loop with a radius of 60 nm can be easily formed by joining side by side the two parts of such open loop.

Compared to the mass fabrication of nanofibres such as nanotubes [2], superconductor wires [14] or inorganic fibre [15], the great advantage of our pulling procedure is that the fibres can be produced one at a time and at a given position on the surface. The positioning precision depends on the end section of the micropipette used which is below 200 nm. After the pulling, we can pick up one extremity of the fibres in the 100 nm range from the surface with a micropipette and move it to another place using the micromanipulator (fig. 3). The smallest radius of curvature at fold is of the order of the fibre diameter. We have also checked that two fibres crossing together do not merge. For nanoscale fibres, manipulations were conducted with an AFM. A nanofibre (fig. 4a)) can be locally deformed (fig. 4b)), cut with the AFM tip (fig. 4c)), opening the way to repositioning by pushing the fibre with the tip apex (fig. 4d)) as in the pushing mode of molecular manipulation with a STM [14], [15]. Thus, a fibre can be shaped arbitrarily ending for example with the formation of a loop with a radius as small as 60 nm (fig. 4e)).

In conclusion, we have demonstrated that drawing can be pushed down to nanometre dimensions, like manipulation [16], [17] and printing [18]. Nanofibres are produced one by one and can be positioned precisely on a surface during their fabrication. Their length which can reach hundreds of microns and their mechanical properties make them easy to use for fabricating a coil or wiring a complex circuit for applications in nano-optics or nano-electronics. The chemical composition is under optimization to improve their optical or electrical properties.

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