Léon Brillouin Laboratory
French Federation of Neutron Scattering

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TRAVELLING ALONG CHANNELS

Confined liquids
seen by neutrons

Editorial

For more than a year now, we've all been experiencing confinement. This unprecedented experience profoundly alters our way of life, our social interactions, our behaviour, our view of the world. At the same time, it also presents new perspectives.

In nature, matter also changes its properties when confined in extremely small volumes. It can change colour or conduct electricity differently. These changes of state take place under different conditions: for example, confined ice melts below 0° C. The confinement of matter is omnipresent in the cells of the living world, in clays and minerals, building materials, new electronic devices or future quantum computers. It plays a crucial role that scientists are trying to understand in order to control it.

What happens when you confine a liquid in channels the size of a few atoms or molecules? How will the liquid flow? How will it interact with the walls? Will it be possible to separate two liquids which, under ordinary conditions, are miscible? From a fundamental point of view, these questions fascinate physicists. Answering them allows applications, from catalysis to biotechnology, including the desalination of sea-water, depollution, and even... cat litter!

Our comic book, illustrated by Aurélie Bordenave, tackles these questions in a playful way, telling the story of a real experiment, carried out by a team of physicists, chemists and technicians in a Very Large Research Instrument (TGIR in French) using neutron diffraction. Neutrons are a fantastic tool for investigating matter at the nanometric scale, the distances between atoms. They can easily penetrate materials and distinguish between isotopes of the same chemical element, such as hydrogen and deuterium. This property makes it possible to change at will the contrast between two liquids, or the contrast with the enclosing material, in order to understand "what's going on inside".

To go from the laboratory world to the nanoworld, physicists send rays, and they use a mathematical tool involving an imaginary intermediate space. However, we have chosen to erase this extraordinarily effective conceptual tool. Instead, our researchers are helped by a cat, which can go directly from our world to that of atoms or molecules. This cat also embodies the scientific mind, by looking critically at these two worlds and their interaction.

But which cat? Ever since Schrödinger's cat, the hero of quantum physics, cats have played a role in science. They also appear in comics, thanks to their mischievousness and independent spirit. Between Geluk's massive cat and the rabbi's skinny cat, many other felines have managed to wheedle their way into the pages of comics. For our comic, we have enlisted the services of Sophie Calle's own cat, called: SOURIS! In French it means both Mouse and Smile, and should remind us to keep smiling in times of trouble.

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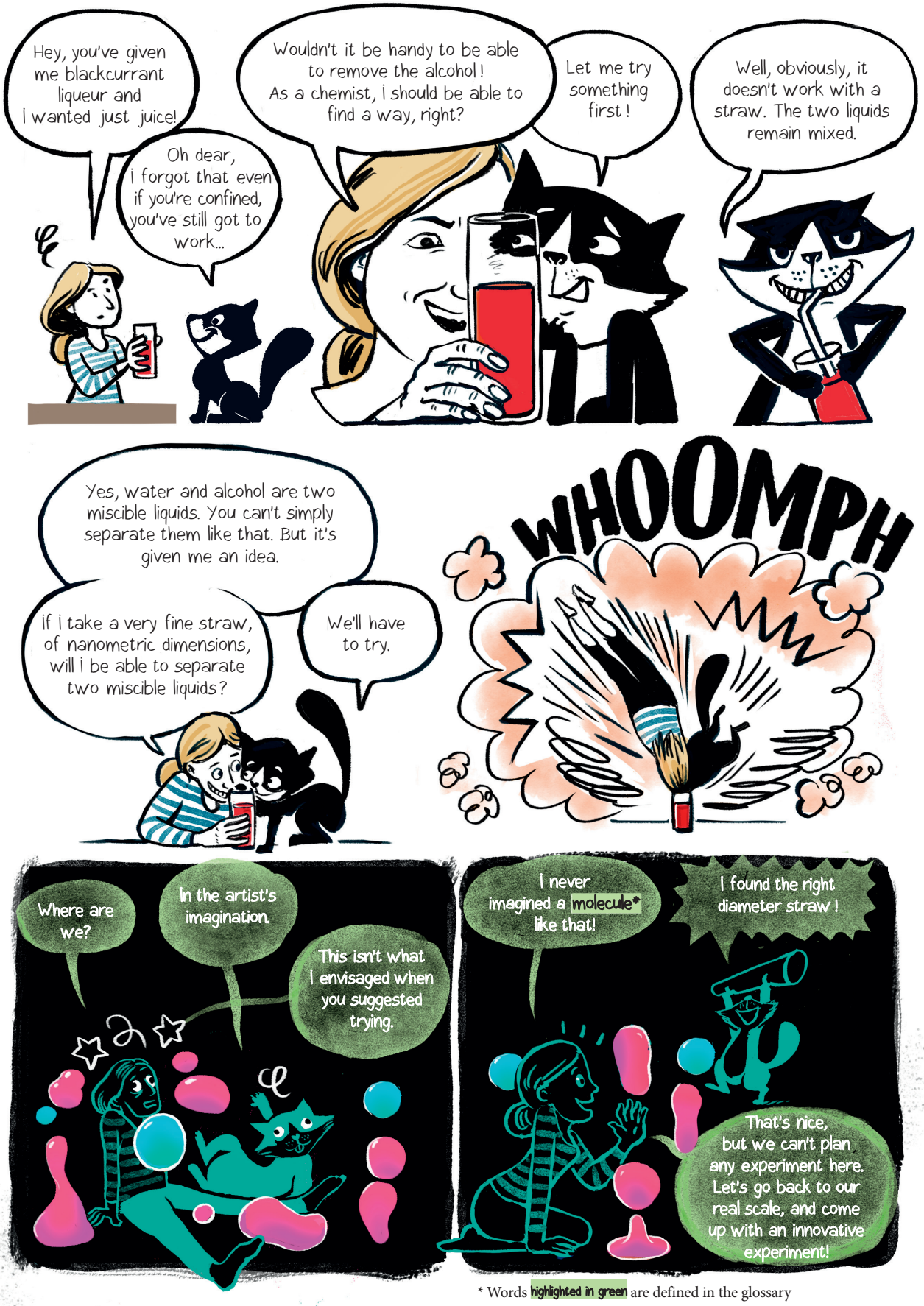
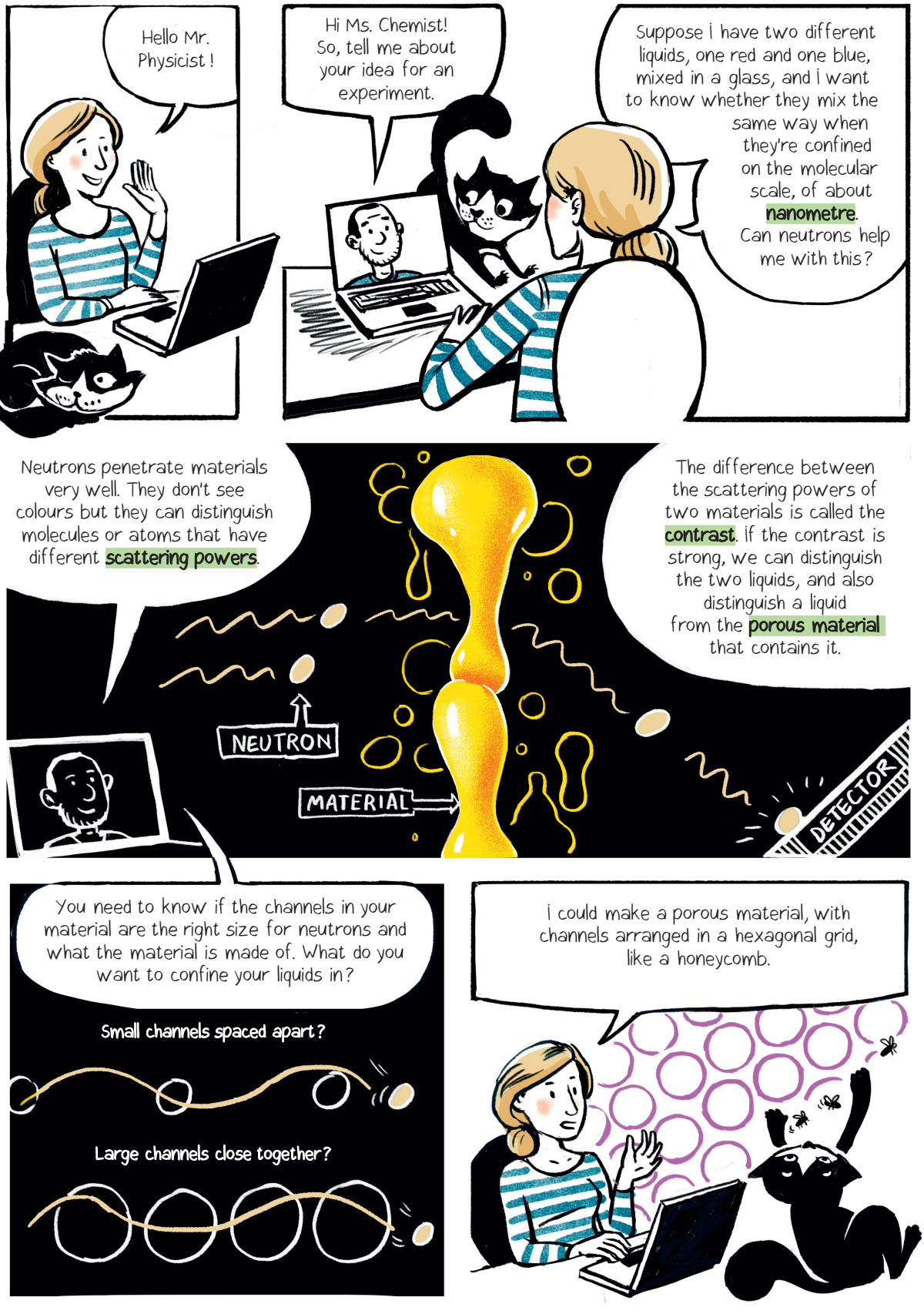
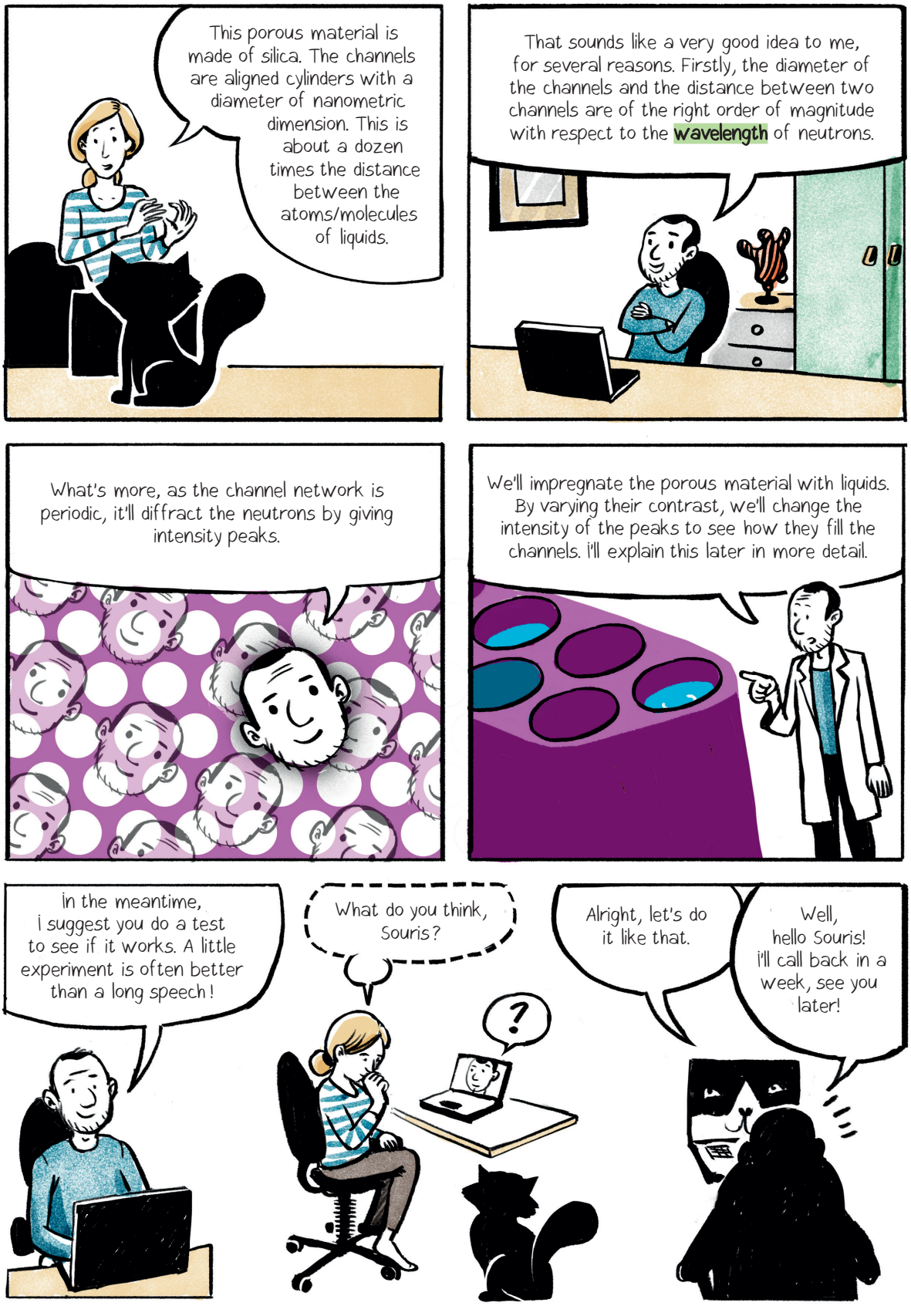
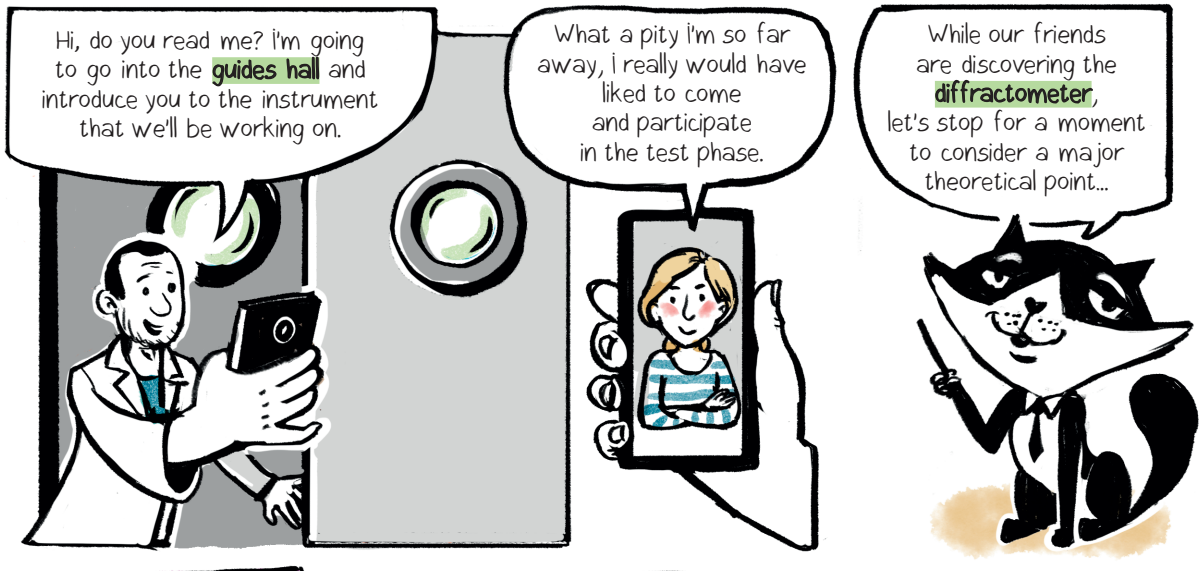
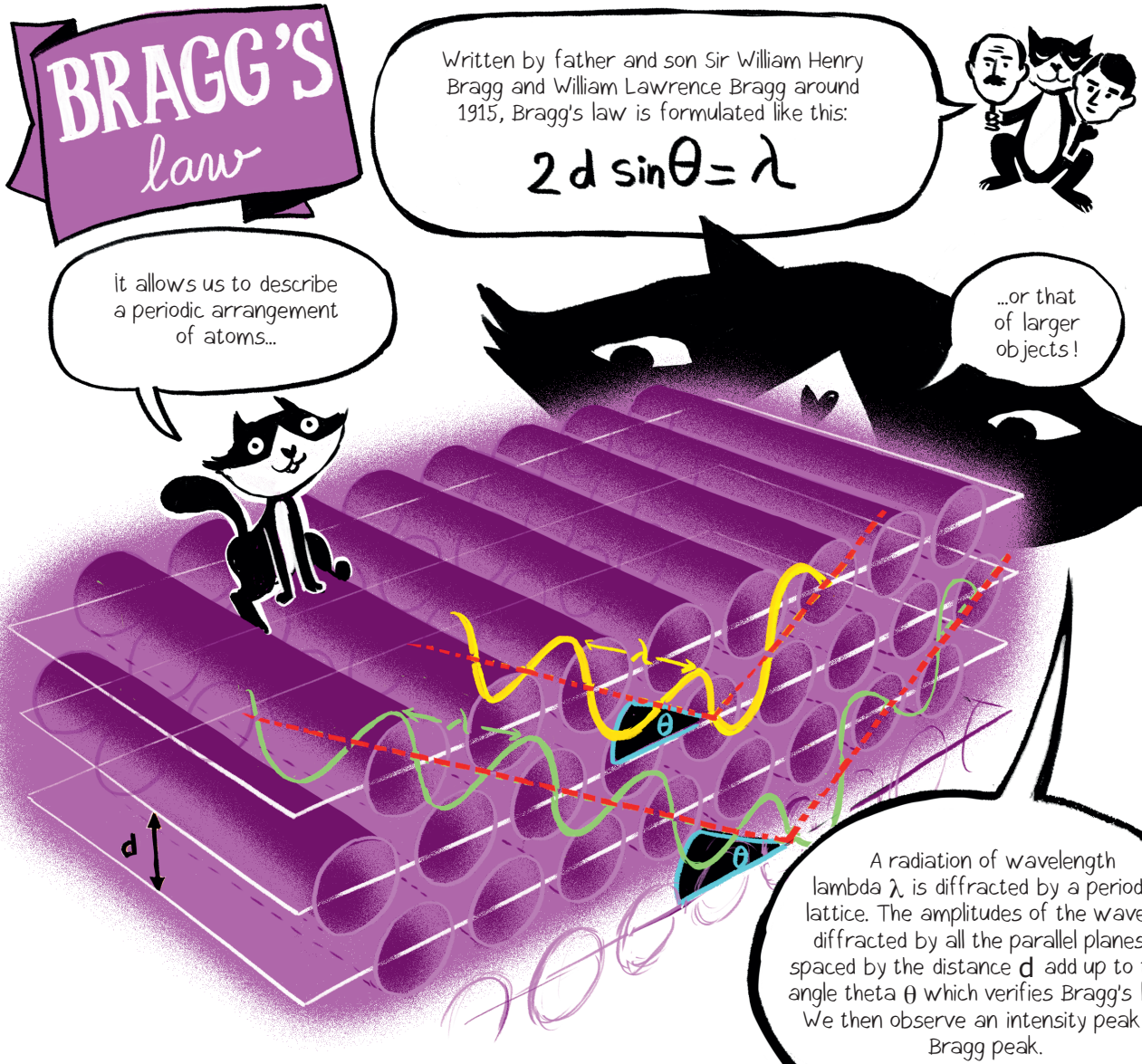


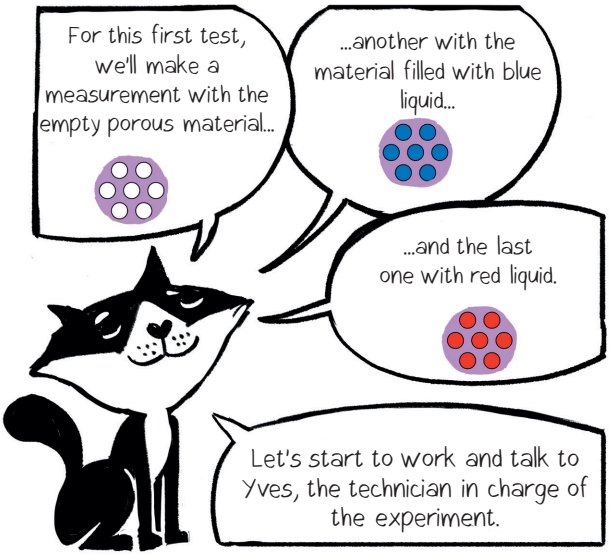
* Words highlighted in green are defined in the glossary

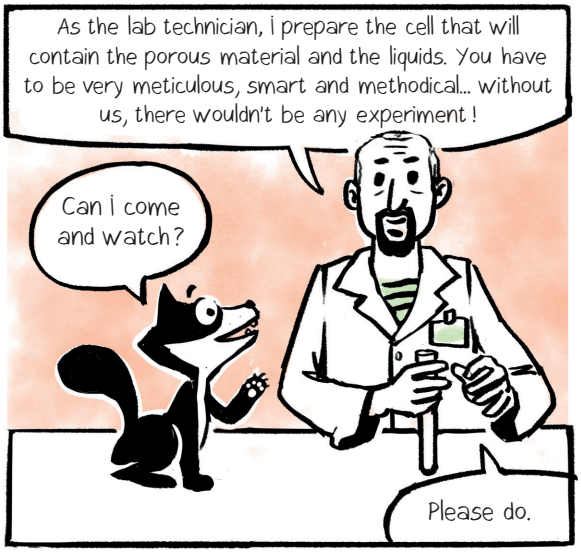

Hello Mr. Physicist!
Hi Ms. Chemist! So, tell me about your idea for an experiment.
Suppose I have two different liquids, one red and one blue, mixed in a glass, and I want to know whether they mix the same way when they're confined on the molecular scale, of about nanometre. Can neutrons help me with this?
Neutrons penetrate materials very well. They don't see colours but they can distinguish molecules or atoms that have different scattering powers.
NEUTRON
MATERIAL
DETECTOR
The difference between the scattering powers of two materials is called the contrast. If the contrast is strong, we can distinguish the two liquids, and also distinguish a liquid from the porous material that contains it.
You need to know if the channels in your material are the right size for neutrons and what the material is made of. What do you want to confine your liquids in?
Small channels spaced apart?
Large channels close together?
I could make a porous material, with channels arranged in a hexagonal grid, like a honeycomb.


This porous material is made of silica. The channels are aligned cylinders with a diameter of nanometric dimension. This is about a dozen times the distance between the atoms/molecules of liquids.
That sounds like a very good idea to me, for several reasons. Firstly, the diameter of the channels and the distance between two channels are of the right order of magnitude with respect to the wavelength of neutrons.
What's more, as the channel network is periodic, it'll diffract the neutrons by giving intensity peaks.
We'll impregnate the porous material with liquids. By varying their contrast, we'll change the intensity of the peaks to see how they fill the channels. I'll explain this later in more detail.
In the meantime, I suggest you do a test to see if it works. A little experiment is often better than a long speech!
What do you think, Souris?
?
Alright, let's do it like that.
Well, hello Souris! I'll call back in a week, see you later!


Hi, do you read me? I'm going to go into the guides hall and introduce you to the instrument that we'll be working on.
What a pity I'm so far away, I really would have liked to come and participate in the test phase.
While our friends are discovering the diffractometer, let's stop for a moment to consider a major theoretical point...

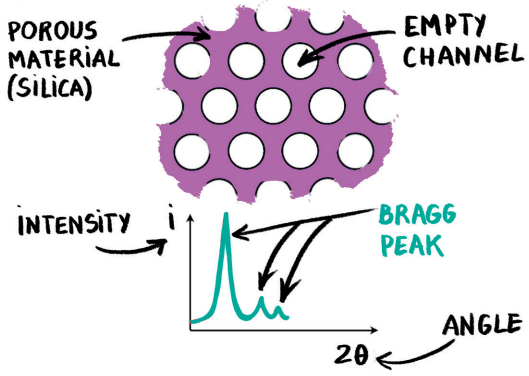

BRAGG'S law
Written by father and son Sir William Henry Bragg and William Lawrence Bragg around 1915, Bragg's law is formulated like this:
$2d\sin\theta = \lambda$
It allows us to describe a periodic arrangement of atoms...
...or that of larger objects!
θ
θ
d
A radiation of wavelength lambda λ is diffracted by a periodic lattice. The amplitudes of the waves diffracted by all the parallel planes spaced by the distance d add up to the angle theta θ which verifies Bragg's law. We then observe an intensity peak or Bragg peak.



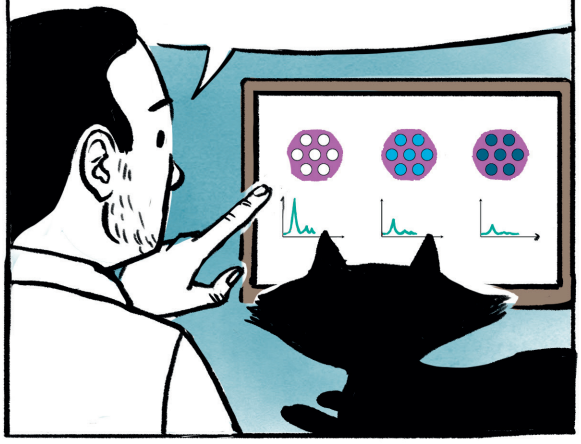


* See the answer to Souris' question at the end of the comic.

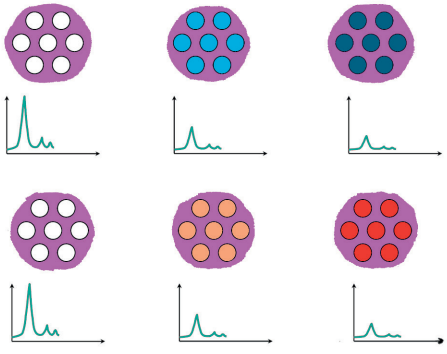
This test confirms our intuition: when the porous material is empty, we obtain very intense Bragg peaks, revealing a high contrast.



When you saw the liquid filling the channel, I could see the intensity of the Bragg peaks decreasing and then stabilizing, once everything was filled.



The same thing happened with the two liquids, the blue and the red. We say that the intensity of the Bragg peaks varies as the square of the contrast.

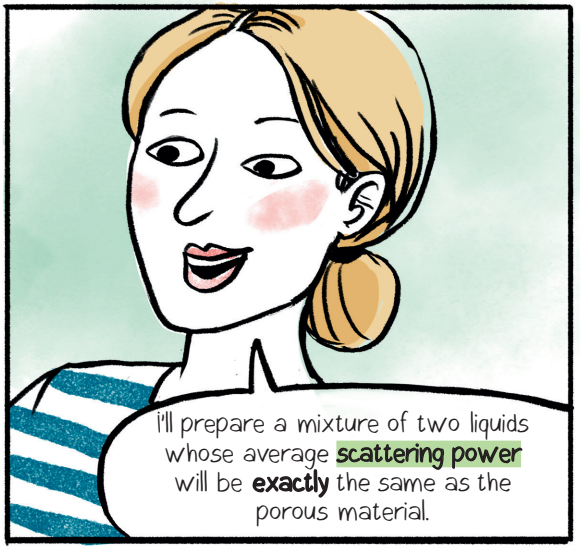


When there's nothing in the channels, there's a strong contrast between the silica and the vacuum. The Bragg peaks are intense. As the channels fill up, the contrast decreases.

We ought to think about the real experiment.

The test is positive, it's time to write a proposal for an experiment!

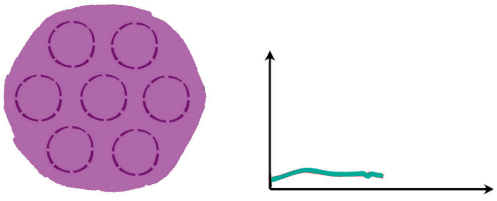
You're right... ... I need to define a scenario and an experiment strategy.



I'll prepare a mixture of two liquids whose average **scattering power** will be **exactly** the same as the porous material.

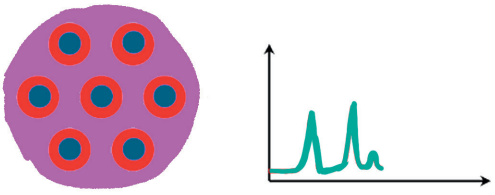
First Hypothesis

if the two liquids mix well, then i'll turn off the Bragg peaks completely, no contrast.



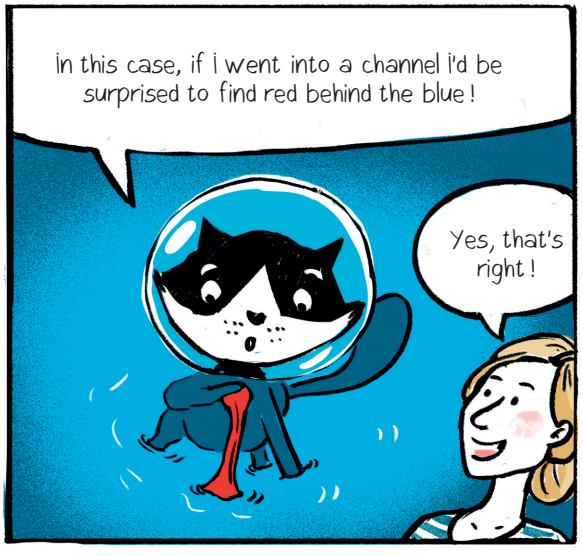
Second Hypothesis

if i do get a contrast, it means that the mixture will have separated into two regions within each channel (crown and core).



in this case, if i went into a channel i'd be surprised to find red behind the blue!

Yes, that's right!

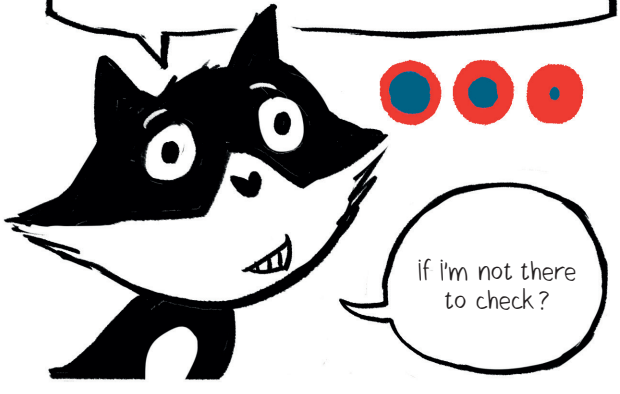


At the risk of asking a silly question, what are blue and red liquids made of?

They are molecular liquids, an alcohol and a hydrocarbon, containing carbon, oxygen and hydrogen. i can vary their contrast (with each other and with silica) by replacing hydrogen with an **isotope**, deuterium.

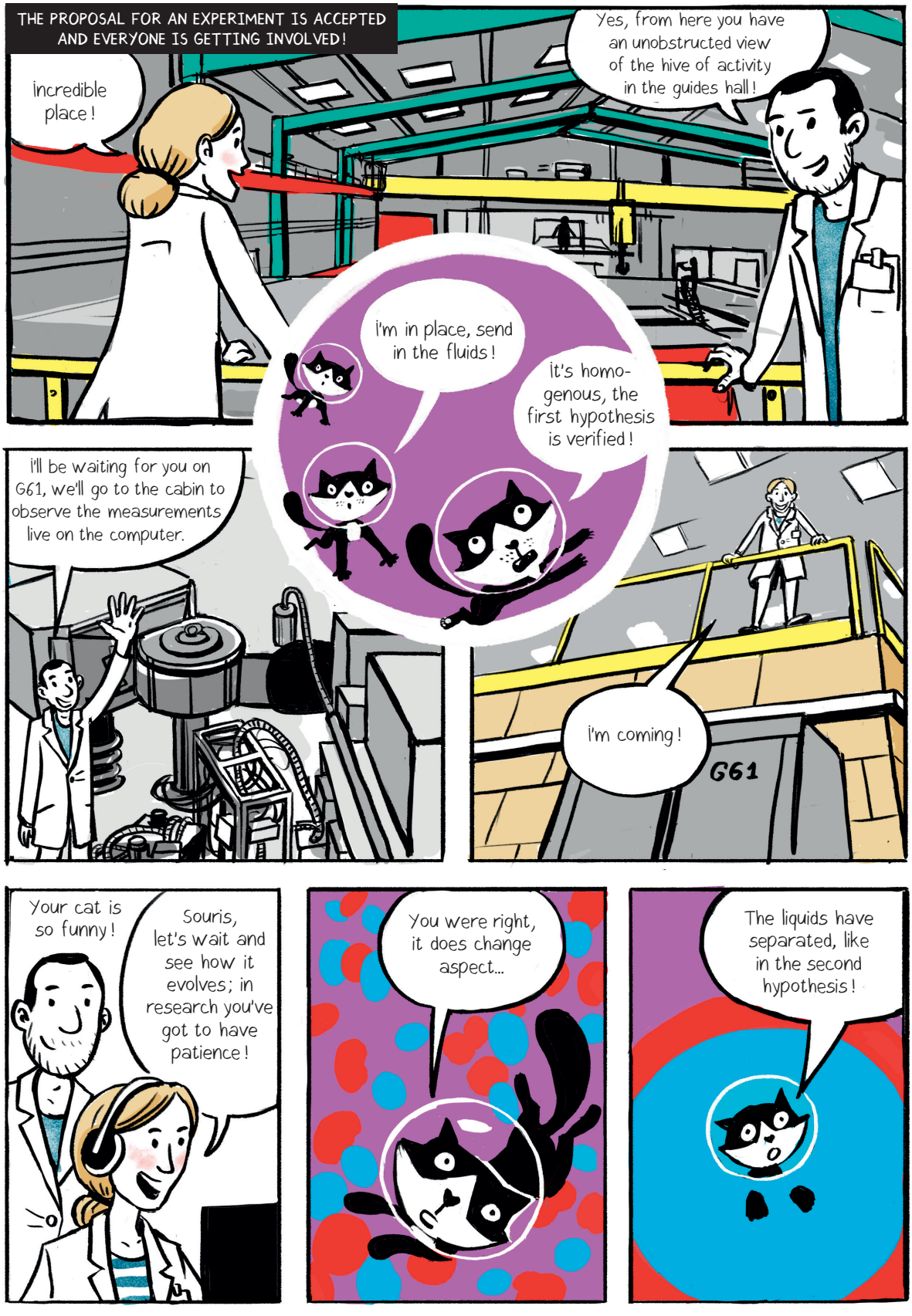
And how will you know exactly how thick the corona and core are? The composition of the liquid in these two areas?

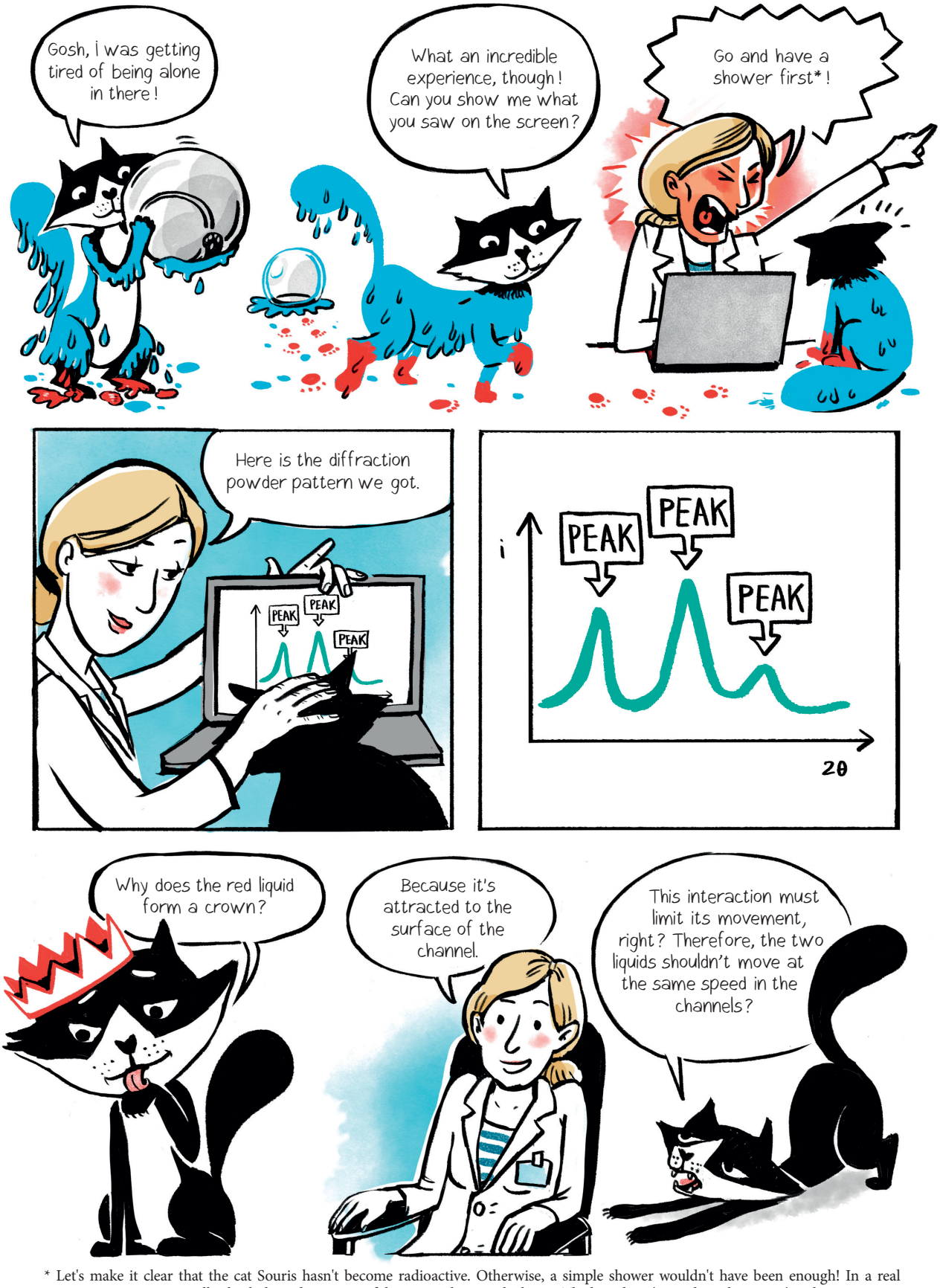
if i'm not there to check?



To determine the exact structure, we'll compare the measured intensities with theoretical models.

i hope this experiment proposal will be accepted!


THE PROPOSAL FOR AN EXPERIMENT IS ACCEPTED AND EVERYONE IS GETTING INVOLVED!
Incredible place!
Yes, from here you have an unobstructed view of the hive of activity in the guides hall!
I'm in place, send in the fluids!
It's homo-genous, the first hypothesis is verified!
I'll be waiting for you on G61, we'll go to the cabin to observe the measurements live on the computer.
I'm coming!
G61
Your cat is so funny!
Souris, let's wait and see how it evolves; in research you've got to have patience!
You were right, it does change aspect...
The liquids have separated, like in the second hypothesis!

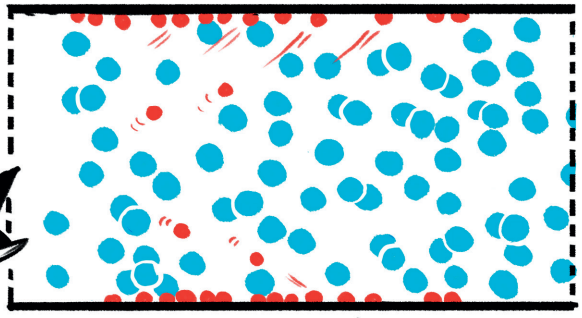


* Let's make it clear that the cat Souris hasn't become radioactive. Otherwise, a simple shower wouldn't have been enough! In a real experiment, we systematically check the radioactivity of the material put in the beam. The liquids we're studying here aren't radioactive.

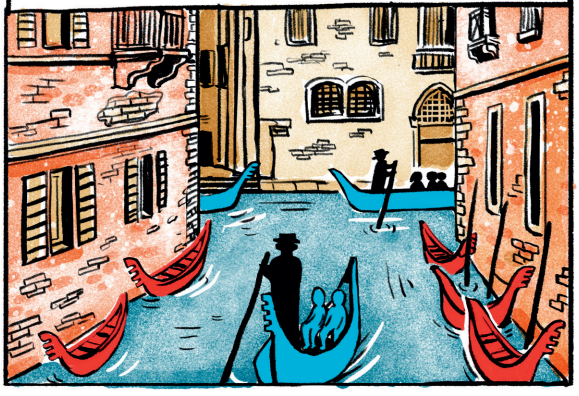
If we measure how the neutron exchanges energy with the material, we'll have access to the movements of liquids.

Great !!!

We can guess that the blue liquid will move faster than the red liquid which is attracted to the surface.



Imagine yourself in Venice. The gondolas in the centre move easily. The ones near the canal banks move much less.
In this metaphor, you're the blue liquid and the moored boats are the red liquid.



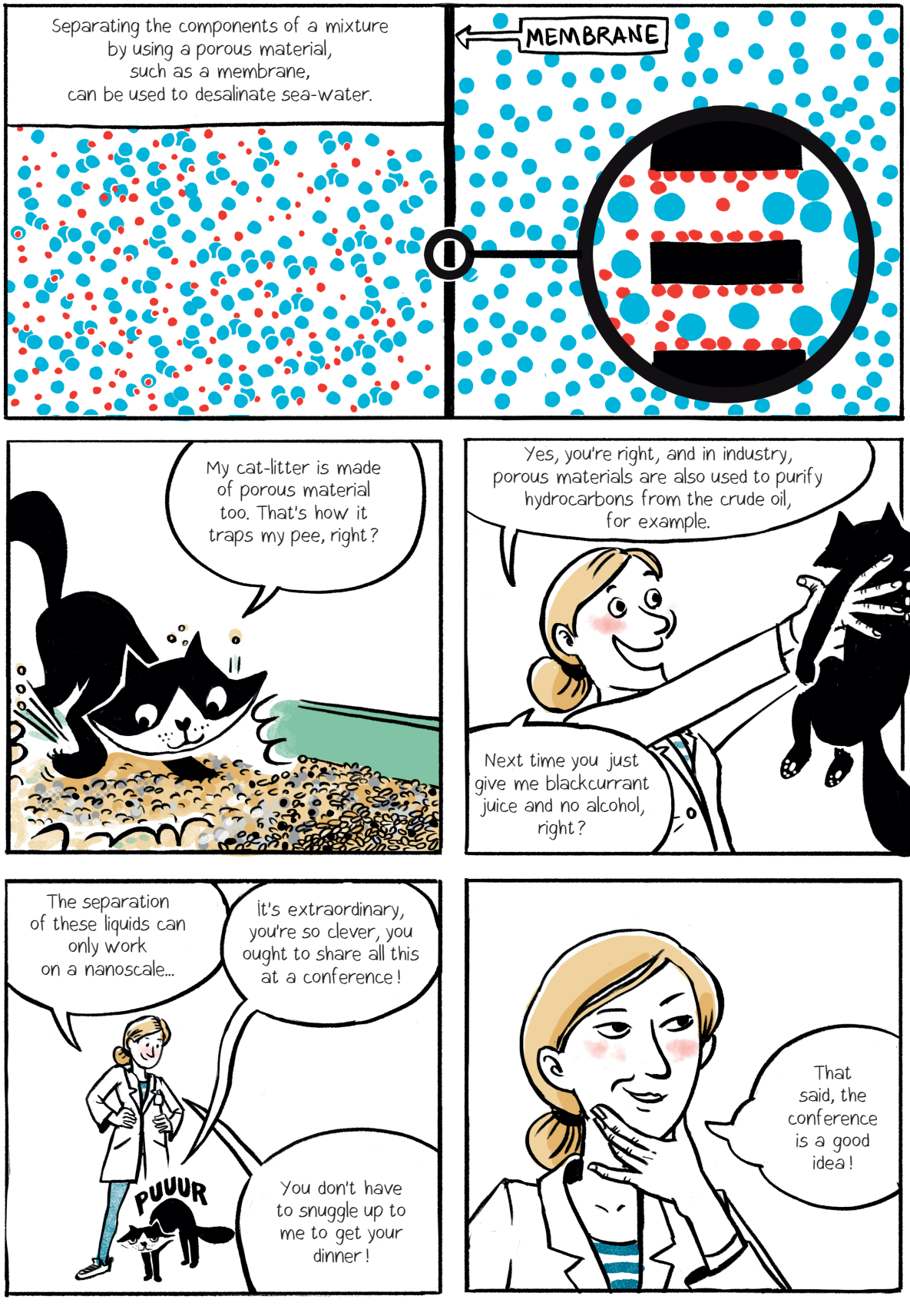
Thanks to the neutrons, we'll be able to follow the movements of both liquids in the channel.

How can we do that? Tell us !

We need to use a **spectrometer** that measures the energy exchanged between the neutrons and the molecules. We could write an experiment proposal for the next committee!.

By the way, what are these first results used for? I've done my bit, I need to know !

Let's see some examples


Separating the components of a mixture by using a porous material, such as a membrane, can be used to desalinate sea-water.
MEMBRANE
My cat-litter is made of porous material too. That's how it traps my pee, right?
Yes, you're right, and in industry, porous materials are also used to purify hydrocarbons from the crude oil, for example.
Next time you just give me blackcurrant juice and no alcohol, right?
The separation of these liquids can only work on a nanoscale...
It's extraordinary, you're so clever, you ought to share all this at a conference!
PUUUR
You don't have to snuggle up to me to get your dinner!
That said, the conference is a good idea!


A FEW WEEKS LATER...
Dear friends, my name is Souris and I am going to present to you my latest adventures inside the channels of a porous material..
What, am I dreaming? He's going to pinch my results now?
I'm the one who's hosting the conference.
MiAOOW
Remember that research is a team effort.
Welcome to our conference which was supposed to take place in the auditorium but...
...since we are now confined, as are the liquids we're going to talk about, I am pleased to meet you live on the web.
I'm going to present the results of the experiments conducted at the Léon Brillouin laboratory. Are you ready?
VODKA
SYRUP

Glossary

Atom - Elementary constituent of matter (solid, liquid or gas). The atom consists of a nucleus of protons and neutrons, and a cloud of electrons.

Contrast - The difference between the scattering powers of two materials. It is used to distinguish between two liquids, or a liquid from the porous material that contains it.

Deuterium - Written as D or ^{2}H, deuterium is a naturally-occurring isotope of the hydrogen atom. It has one proton and one neutron, unlike the more common isotope known as H or ^{1}H, which has a proton but no neutron. Therefore it is heavier, but remains the same chemical element.

Diffractometer - An instrument which selects a beam of neutrons, directs it onto the material to be studied and collects the diffracted neutrons. There are two different types of instruments: the diffractometer measures only the number of neutrons diffracted depending on their direction; the **spectrometer** also measures their energy.

Guides hall - An experimental hall adjacent to a neutron source building, where the instruments are housed and experiments are carried out. The neutrons are conducted from the neutron source to the instruments in tubes several tens of metres long, called guides.

Isotope - Isotopes of an atom have the same number of protons, but a different number of neutrons. Two isotopes therefore have different physical properties (such as mass or scattering power) but are the same chemical element.

Isotopic contrast - The difference between the scattering powers of two isotopes. The isotopic contrast obtained by replacing some hydrogen atoms in a material with deuterium atoms is often used in neutron scattering. There are various possibilities for substitution for other atoms.

Molecular liquid - A liquid made up of molecules. The two liquids used in our actual experiment are an alcohol, tert-butanol, and a hydrocarbon, toluene.

Material - A solid or liquid object made up of a collection of atoms and/or molecules.

Porous material - A solid material with empty cavities, which can be impregnated with a liquid or gas. The cavities in the porous material used in this study are aligned and nano-sized, hence the name nanochannels.

Molecule - An assembly of electrically neutral atoms; the atoms are connected to each other by chemical bonds. Example: the water molecule H_2O.

Nanometre - A unit of length corresponding to one billionth of a metre, (10^{-9}m) which corresponds to the typical distances between atoms in materials.

Neutron - A particle that makes up the nucleus of atoms (along with the proton). Emitted during a nuclear reaction, neutron beams are used to study condensed matter (solid or liquid).

Powder - Porous material is a powder, i.e. it is composed of small crystals, the grains of powder, ranging from a few hundred nanometres to several microns. Within each grain the channels are regularly aligned in a hexagonal lattice. The grains are oriented in all directions in space.

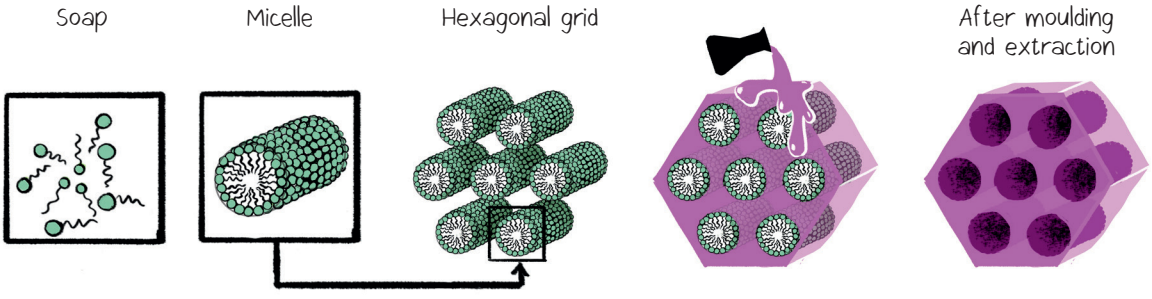
Scattering power - The ability of an atom or material to scatter the neutron beam by changing its direction (according to Bragg's law). It modulates the amplitude of the scattered wave and hence the intensity of the Bragg peaks. Isotopes of the same atom have different scattering powers. Hence, isotopic substitution allows the contrast to be varied.

Wavelength - In physics, a beam of neutrons travelling at the same speed can be represented as a wave, that is, a vibration which has a succession of peaks and troughs, like ripples on the surface of the water. The wavelength is the distance between two successive peaks, and is typically between 0.1 and 1 nanometre for neutrons used in research.

How is the porous material made ?

Molecules with a hydrophilic (water-loving) head and a hydrophobic (water-hating) tail are dissolved in water. These molecules are called amphiphilic, like soap molecules. To interact as well as possible with water, they spontaneously organise themselves into long rods, called cylindrical micelles. The micelles arrange themselves to form a hexagonal network.

This network is imprinted by moulding a solid material, called silica, around the micelles. After extraction of the micelles, a porous material is obtained with a hexagonal structure like a honeycomb.



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TRAVELLING ALONG CHANNELS

Confined liquids as seen by neutrons

A cat and its owner explore channels, dug in a porous material, and filled with liquids. This journey, with many twists and turns, leads them to discover the fascinating properties of confined liquids, revealed by the radiation of a neutron source.

These properties have applications, for example in desalinating sea-water. Captured on the spot by the comic strip, their adventure follows the story of a scientific research project, which requires imagination on their part, risk-taking, collaboration and critical thinking. Confinement also has its advantages !

TO FIND OUT MORE

ABOUT CONFINED LIQUIDS

- JDN 14 - *Surfaces, Interfaces, Confined Media by Neutron Scattering.* Murol, France, May 2006
  A. Brûlet and G. Chaboussant - ISBN : 978-2-7598-0022-3
- Bio-inspired inorganic and hybrid materials, Clément Sanchez (2012), **mediachimie.org**/ressource/matériaux-inorganiques-et-hybrides-bio-inspirés

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- Comic book: *Let's Scatter Neutrons* (2018)
- Booklet *Le LLB au quotidien - Daily Life at the LLB* (2019)
- *Spin Ice: the experiment* (2020)