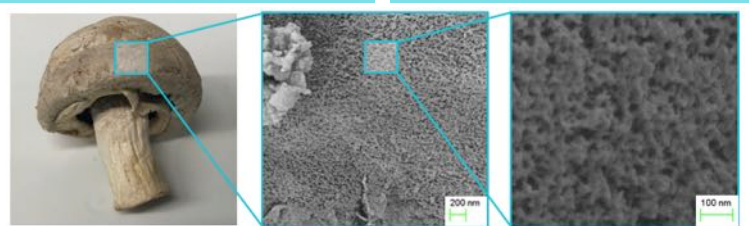


WWW. KNIFE  FELIX .DE

ACCOMPANYING MATERIAL FOR THE EXPERIMENT WEBSITE WWW.KNIFFELIX.DE ON THE SUBJECT OF

AEROGELS

Research for our everyday lives

WHAT	HOW
	
WHERE	WHO

FUNDING



Federal Ministry
of Education
and Research



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COOPERATING RESEARCH INSTITUTE



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TARGET AUDIENCE

Ages 14-99+

Individuals
School Classes
Students
Cooperators



ENGLISH VERSION

TUHH
Hamburg
University of
Technology



Structure of the documents:

For Schools:	Teaching Manual
For All:	Basic Knowledge Experiments Advanced Material Exkurses Career Education & Study Orientation

www.kniffelix.de is the free hands-on experiment website created by the TUHH's KinderForscher junior researcher initiative www.kinderforscher.de. The aim of the initiative is to make science, technology and research accessible to everyone: From everyday life to experimentation to research and career guidance.

Kniffelix.de has been awarded the Seitenstark seal of approval for recommended digital children's media.

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Contents of the accompanying documents

This is how the materials are structured:

- Basic Knowledge 1: Aerogels and gels
 - Experiments: Making and drying hydrogels
 - Excursus 1: Can we produce aerogels by air drying?
- Basic Knowledge 2: Production of aerogels
 - Excursus 2: Raw materials for aerogels - the example of biopolymers
 - Excursus 3: Hydrogel formation - example of gelation of alginate (egg-nesting mechanism)
 - Excursus 4: Solvent replacement
 - Excursus 5: Supercritical drying explained using the phase diagram
- Basic Knowledge 3: Structure, properties and applications of aerogels
 - Excursus 6: Interesting facts about pores
 - Excursus 7: Study orientation in the field of aerogels

The documents Basic Knowledge 1 to 3 each provide an overview of the topic.
The experiments and excursions provide opportunities for in-depth study.

Teaching Manual: Aerogels

Objectives of the teaching unit:

- Gain insights into the production and application of aerogels
- Research what aerogels are used for
- Experimentation: Making and drying gels, measuring and documenting changes in volume
- Learning that, in addition to the known states of matter, there is also the supercritical state and what advantages this offers
- Career education & study orientation - from bachelor's degree to postdoctoral lecturer or professor
- Get to know aerogels and their importance or limitations as insulating materials

Reference to the curriculum for teaching a practical training course in natural science for schools in Hamburg

Topic: From raw materials to products

Knowledge:

- Describe the manufacturing process

Gaining knowledge:

- Investigate properties and reactions of substances based on hypotheses
- Tracing the path from raw materials to end products as an example
- Apply the substance-particle concept to explain changes in substances

Communication:

- Recording test results
- Researching topic examples

Rating:

- Evaluate materials and their production processes from an economic and ecological point of view

Correlation to the chemistry curriculum in Hamburg for grades 11-13

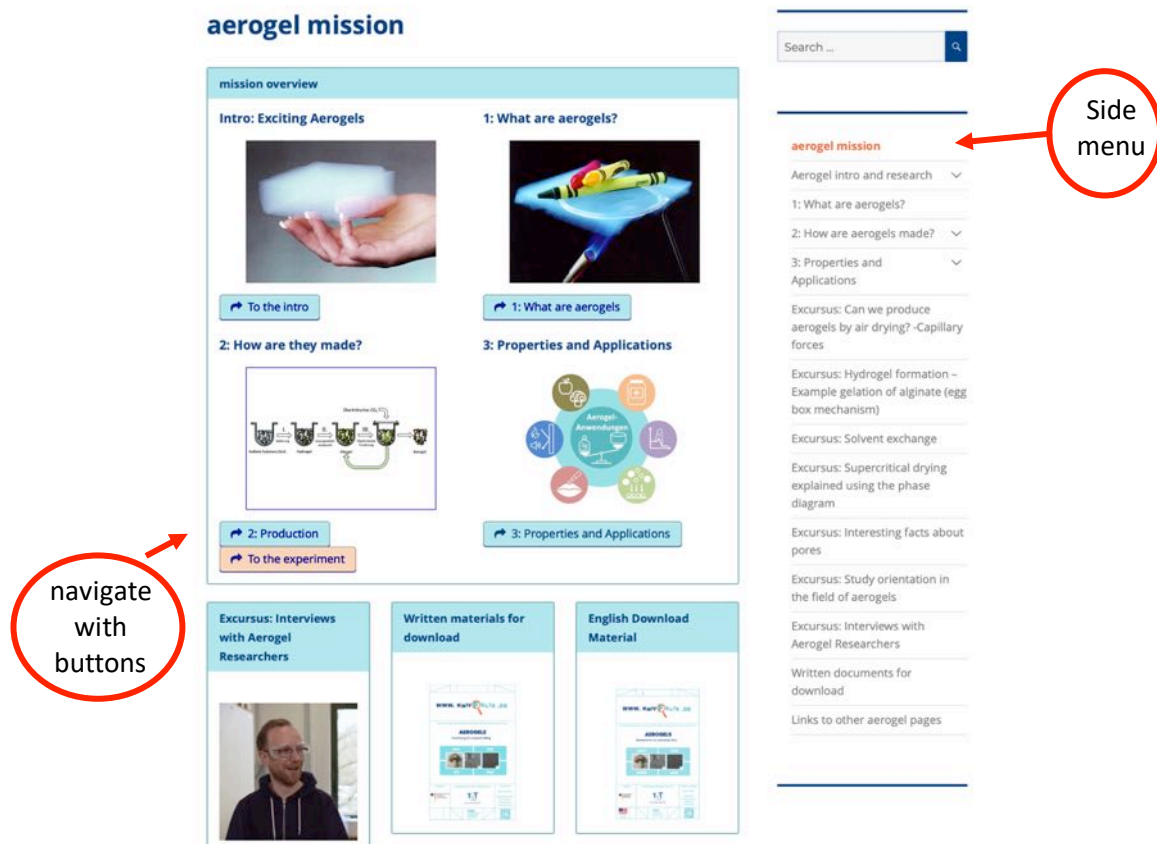
Here, the topic can be integrated into the following contexts:

- Organic chemistry
- Natural macromolecules (carbohydrates, proteins, fats)
- Modern materials and chemical products

The topic also offers study and career guidance.

The Kniffelix platform www.kniffelix.de offers a free digital teaching unit with lots of information, puzzles, experiments, interviews and interactive videos. Users can also ask the researchers questions. Kniffelix can be used with PCs/laptops, tablets and smartphones. The aerogel mission can be accessed via the menu with the puzzle topics or via the corresponding tile on the start page. Navigation within the unit is done using buttons to move from task to task or via the side menu of the mission, which can be used to access specific content, see figure 1.

As far as the experiments are concerned, aerogels cannot be made at school, but the starting materials are gels such as jelly, Jello or alginate gels, which can be made in the classroom or science room or even at home without much effort (see also the "Notes on the experiments" written in red in the next section). These gels can then be dried, and the pupils will notice that they shrink. They have produced so-called "xerogels". They will then learn why "supercritical drying" aerogels does not cause shrinking, retaining the structure of the gel after drying, making applications of aerogels especially interesting.



aerogel mission

mission overview

Intro: Exciting Aerogels

1: What are aerogels?

2: How are they made?

3: Properties and Applications

Excursus: Interviews with Aerogel Researchers

Written materials for download

English Download Material

Search ...

Side menu

aerogel mission

Aerogel intro and research

1: What are aerogels?

2: How are aerogels made?

3: Properties and Applications

Excursus: Can we produce aerogels by air drying? -Capillary forces

Excursus: Hydrogel formation - Example gelation of alginate (egg box mechanism)

Excursus: Solvent exchange

Excursus: Supercritical drying explained using the phase diagram

Excursus: Interesting facts about pores

Excursus: Study orientation in the field of aerogels

Excursus: Interviews with Aerogel Researchers

Written documents for download

Links to other aerogel pages

navigate with buttons

Figure 1: Navigation options for the Aerogel mission on the Kniffelix-Website

You can gather the experiment materials yourself. The written materials can be downloaded as a PDF document within the aerogel learning mission or via the menu-tab „For teachers“

Students get a good overview with the documents referred to as basic knowledge: "Basic knowledge 1" about gels, aerogels and their interesting invention history, "Basic knowledge 2" about the production of aerogels and "Basic knowledge 3" about the structure, properties and applications of aerogels.

The excursions are additional materials that take you even deeper into the topic. Excursus 1 explains why gels shrink during a normal drying process. Excursus 2-5 explain details mentioned during the manufacturing process. Excursus 6 explains why the pore structure is so important for an aerogel, and finally, Excursus 7 presents various courses of study and levels at which one can work with aerogels.

The texts of the written materials are also included in the missions on the platform and are enriched with interactive quizzes and videos. They can therefore be used directly on the platform or - if internet access is not available - in the print version in English or German.

1. Suggestion for the first teaching unit:

Introduction:

The unit can be introduced with the following sentences: "This lesson is about aerogels. These are superlight materials with fascinating properties. Research is being carried out at Hamburg University of Technology into what they can be used for and how they can be produced even better. With the Kniffelix learning platform, they let us take part in this."

To get you in the mood, you can watch the intro movie of the mission (go to www.kniffelix.de, in the menu "Puzzle topics", select the Aerogel mission and click on "Go to intro"). The pupils can then work through the learning missions at their own pace, or you can target specific content.

If you also want to carry out the experiments, it is advisable to do them in the first or second lesson after the introduction, so that the pupils can first experience the problems involved in aerogel production, namely the shrinking of the gels, for themselves.

Information about the experiments:

Aerogels are created by drying gels in a special way, which cannot be done without special equipment. However, gels can be produced in a kitchen or classroom and dried conventionally, causing them to shrink. This provides a basic understanding of the need for special supercritical drying, retaining the gels' structure.

Gel production: Gels can be produced from starch, jelly, agar-agar and alginate, for example (see experiment instructions). On the Kniffelix.de platform, the gelation of sodium alginate with calcium chloride is shown in videos. These materials can be purchased by mail order. The other materials are available from grocery stores. You can either limit yourself to one type or let the groups try different materials. Most of them gel when exposed to heat, only alginate gels when ions are added.

Gel drying: Gel drying can be carried out at room temperature over several days to weeks or more quickly in the oven. However, jelly and agar-agar will become liquid again. Only starch and alginate gels can be dried in the oven with some dimensional stability, but with shrinkage.

Basic Knowledge 1: Aerogels and Gels

What are Aerogels?

Aerogels are **the lightest solids in the world** because they are essentially made of air (up to 99.98%!!!). You can think of them a bit like foam that has solidified, but with much more air and such fine pores that some aerogels are almost transparent. They are therefore also referred to as "frozen smoke" (see Fig. 1). The air content in Aerogels is so high that there are not just individual holes like in Swiss cheese, but the **pores form a cave system** (Fig. 2). Due to the large amount of trapped air, aerogels are **extremely heat and sound insulating!** If you place crayons, chocolate or ice cubes on an aerogel plate over a flame, they will not melt (Fig. 3). Once you've seen and felt an aerogel like this, you'll be fascinated!

But so far, only a few people have had the opportunity to see or feel aerogels, as they are high-tech materials that are produced in a complex process. This requires a lot of research and the materials are expensive. Good ideas are needed on how to produce the materials more cheaply and develop marketable products from them. We would like to take you along on this exciting process!

How were aerogels invented?

It all began with a bet made by chemist Samuel Kistler in 1931. He was fascinated by the wobbly consistency of gels such as jelly, and bet a colleague that he could remove the liquid from it without it losing its shape, which he succeeded in doing. You will find out how to do this later. Now let's first clarify what gels (or more precisely hydrogels) are, because they are needed as starting materials for aerogels.

What are Gels and what are Hydrogels?

Gels are substances that are frequently found in medicine and cosmetics, in food, but also in nature, see Figure 4. You are familiar with hair gel, raspberry jelly, Jello, perhaps also a gel filled saddle on a bicycle or soft contact lenses. Examples of gels in nature are mucus, fats, jellyfish and the vitreous humor in the eye.

Under very high magnification (a light microscope is not sufficient), you can see that gels are solids with pores that are usually filled with liquid, similar to a sponge. The liquid is located.

The liquid is so firmly trapped in the pores that it cannot simply run out. The pores are interconnected so that the solid and liquid permeate each other. As the solid and liquid do not dissolve in each other, a gel is also referred to as a heterogeneous mixture.

The term "gel" is often associated with a flabby consistency and a translucent appearance like jelly or jellyfish.

In a **rather broad definition**, but one that fits the aerogels described here, fruits and vegetables, indeed all plants, can also be regarded as natural gels, because they also consist mainly of **network-like solids in which liquids are bound**. They just have a more complex structure because they contain cells that can be seen

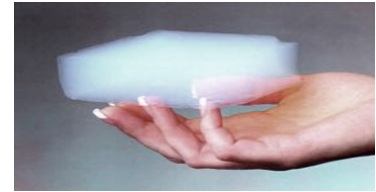


Figure 1: Aerogel (Source: Courtesy NASA/JPL-Caltech – NASA Stardust Website, license: CC0 1.0)

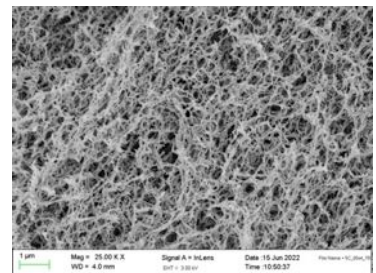


Figure 2: This is what the net type of structure of a strongly magnified aerogel can look like.

(Source: Institute of Thermal Process Engineering)



Figure 3: The aerogel plate isolates



Figure 4: Examples of gels

under a light microscope, whereas the structure of gels in the narrower sense - as already mentioned is not visible under a light microscope, otherwise they could not be transparent. These gels in the narrower sense consist of cross-linked macromolecules, e.g. carbon, silicon or metal-based polymers, starch, protein or fats.

In technical jargon, a gel is called a **hydrogel** (from the ancient Greek hydōr "water") if the liquid contained in the pores is water, see Figure 5. In an **alcogel**, the pores contain alcohol. However, if the pores are filled with air, it is called "**aerogel**", because aero is derived from the ancient Greek word aéros and means "air". The word **aerogel** directly translated means nothing other than "air gel".

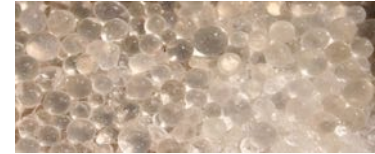


Figure 5: Hydrogels in bead form
<https://commons.wikimedia.org/wiki/File:SilicaGel.jpg>

From these explanations you can already guess that **aerogels** are characterized by a special drying of **hydrogels**, as most drying processes cause the gels to shrink or break down completely. These dried shrunken gels are called **xerogels**.

One more remark: Aerogels are not a class of materials like metals or plastics. Aerogels can be produced from many different materials, from thickening agents used in the kitchen such as starch and gelatine, but also from silicon compounds (these are the most common), from plastics and metals. At the Institute of Thermal Process Engineering at the Hamburg University of Technology (TUHH), aerogels in particular are produced from renewable raw materials, so-called **biopolymers**.

Overview of the further material:

You can find out more about aerogels in the following documents. They are divided into basic knowledge and excursions and can be read independently of each other. "Basic Knowledge 2" is about the production of aerogels and "Basic Knowledge 3" is about the structure, properties and applications of aerogels.

The excursions are additional materials that take you even deeper into the topic. Excursus 1 explains why gels shrink during a normal drying process. Excursus 2-5 explain details mentioned during the manufacturing process. Excursus 6 explains why the pore structure is so important for an aerogel, and finally, Excursus 7 presents various careers, courses of study and levels in which one can work with aerogels.

- Basic Knowledge 1: Aerogels and gels
 - Excursus 1: Can we produce aerogels by air drying?
- Basic Knowledge 2: Production of aerogels
 - Excursus 2: Raw materials for aerogels - the example of biopolymers
 - Excursus 3: Hydrogel formation - example of gelation of alginate (egg-nesting mechanism)
 - Excursus 4: Solvent replacement
 - Excursus 5: Supercritical drying explained using the phase diagram
- Basic Knowledge 3: Structure, properties and applications of aerogels
 - Excursus 6: Interesting facts about pores
 - Excursus 7: Study orientation in the field of aerogels

Experiment 1: Making Hydrogels

There are various gelling agents in the kitchen that can be used to make hydrogels. Example of gelling agents of animal origin are gelatine and Jello. Gelling agents of plant origin such as starch, agar-agar and sodium alginate, are further examples. The easiest way to make hydrogels is with gelatin and hot water, as hot water from the kettle is enough to cause gelling. If you also have a hotplate available, you can make starch and agar-agar gels. For sodium alginate gels, you need sodium alginate and calcium chloride, which can be ordered by mail order. This preparation does not require heat but does require an electric mixer or food processor.

Equipment and ingredients needed:

- **Ingredients for a Jello or Gelatin:**
 - 1 package Jello
 - 1 tablespoon sugar (only if you want to try it later, better leave it out for the **aerogel** production)
 - 1 tablespoon for measuring
 - 1 spoon or similar for stirring
 - 125 ml water
 - Electric kettle to make hot water
 - Measuring cup (to measure 50 ml and 75 ml of water)
 - 1 bowl for Jello
 - 1 ice cube tray to leave to cool or a bowl and a knife
- **Ingredients for a Starch-Gel:**
 - 25 g starch (corn- or potato starch - or both, to compare)
 - Hotplate/stove with small pot and whisk
 - Measuring cup (for 100 ml water) or scale for 100 g water
 - 1 ice cube tray to leave to cool or a bowl and a knife
- **Ingredients for an Agar-Agar-Gel:**
 - 1 packet of agar-agar
 - 1 tablespoon sugar ((only if you want to try it later, better leave it out for the **aerogel** production)
 - Hotplate/stove with small pot and whisk
 - 1 ice cube tray to leave to cool or a bowl and a knife
- **Ingredients for an Alginate-Gel:**
 - 15 g sodium alginate and 1/2-liter water
 - 25 g calcium chloride and 1.5 liters of water
 - An electric mixer or food processor
 - 2 large containers for at least 0.5 or 1.5 liters of liquid
 - 1 disposable syringe (without cannula) or a cake icing syringe

If you want the gels, which gel with heat, to set quickly, you can leave them to cool to room temperature after heating and then put them in the fridge.

Preparing Jello or gelatin:

Put 1 pouch of Jello or gelatine (and 1 tablespoon of sugar if you want to eat it) in a bowl and mix with 50 ml of hot water until everything is dissolved. Then add 75 ml of cold water. Pour the liquid into an ice cube mold and let it cool and solidify (it's faster in the fridge). You can also leave it to set in the bowl and then cut into even cubes.

Preparing the starch gel:

Mix 25 g potato or corn starch with 1 tbsp cold water. Bring 100 ml water to boil in a pot on the stove. Pour the mixed starch mixture into the hot water and boil for half a minute, stirring constantly! Then pour mixture into cube tray and leave to cool (at room temperature or more quickly in the fridge).

Preparing the agar-agar gel:

Pour 250 ml of water into a pan and stir 3 g or approx. 1.5 tsp of agar agar and sugar (2 tbsp?) into the still cold liquid. Bring the mixture to the boil and simmer on a medium heat for about two minutes. Then pour into the ice cube mold and leave to cool (at room temperature or more quickly in the fridge). Note: Unlike traditional cake icing, agar-agar only solidifies when it cools.

Preparing the alginate gel:

You need to prepare two solutions for the experiment: an alginate solution and a calcium chloride solution. By dripping the alginate solution into the calcium chloride solution, solid gel beads are formed.

Safety instructions for handling calcium chloride:



Causes serious eye irritation.

In case of contact with eyes: Rinse cautiously with water for several minutes. Remove any contact lenses if possible. Continue rinsing.

a) Preparation of alginate solution

Add 15 g of alginate powder to half a liter of water. Alginate does not dissolve easily, so you should use a blender / food processor or similar. Stirring vigorously with a whisk will certainly also work, but it will certainly take longer, and lumps may form! As the alginate dissolves, the solution will gradually become more viscous: when it is clear and viscous, you are done. Sometimes a few lumps of alginate form that are particularly difficult to dissolve. If necessary, you can fish these out of the solution with a tablespoon.

b) Preparation of calcium chloride solution

Add 25 g of calcium chloride powder to 1.5 liters of water and stir with a whisk/spoon for a short time until the calcium chloride is completely dissolved. This normally takes a few minutes, as calcium chloride is easily soluble in water.

You can now gel the alginate solution: The easiest way is to gradually drip the alginate solution into the calcium chloride solution, e.g. using a syringe from the pharmacy or a cake icing syringe. Depending on how you drip the alginate solution, you can create different gel shapes. Try to make perfectly round particles like the picture in mission 2e. If you are unsure, you can watch the video on alginate production there in the mission (e.g. using the QR code: Video gelling).



Video gelling

You have now completed the first step of alginate aerogel production and obtained an alginate hydrogel. You can then simply fish or sieve the particles out of the solution.

Experiment 2: Drying Hydrogels

Experiment execution:

Take the gels from experiment 1 and try to dry them without them shrinking. This can either be done in the air (takes several days) or in the oven. You may also be able to think of other options. We have dried gels and fruit in the oven for 4 hours at 70 °C circulating air and dried gels for 9 hours at 50 °C with the fan on, on a baking tray lined with baking paper.

Important: First think about how you want to evaluate the experiment (see section "Evaluation" below). You should measure your hydrogels before and after drying and preferably also photograph them.

Note:

In addition to the "glibbery" gels, you can also use fruit, which has also bound a lot of moisture. For example, like this:

Peel an **apple** or a piece of **cucumber** and cut out an approx. 2x2x2 cm cube-shaped piece. If you want to use **grapes** or **blueberries**, you can use them whole. **Bananas** should be peeled and cut into even slices about 2 cm thick.

Evaluation:

1. Describe: How do your gels behave when drying?
2. Measure how the length, width, height and weight change over time. You can also calculate the volume from the length, width and height and see how it changes.
3. Present your results in a protocol. You can download our sample protocol for this purpose.
4. Look at the results. Have you managed to avoid shrinkage?



Test Protocol: Drying **Hydrogels**

Task:

How do your gels behave when drying? Measure how the length, width, height and weight change over time. You can enter your results in the bold columns of this table. In the thinly printed columns, you can calculate how the value has changed compared to the initial value, as this is the decisive factor. You can then enter these values in a diagram.

Sample (Type of gel):					Type of drying:				
Date, Time	Hours since start of trial	Length	Change in length	Width	Change in width	Height	Change in height	Weight	Change of weight

Have you managed to avoid shrinkage? _____

Excursus 1:

Can we produce aerogels by air drying?

When gels are dried in the air, the liquid in them evaporates and the gel shrinks (see Fig. 1). We are also familiar with this phenomenon from fruit. The reason for this is that capillary forces contract the gels so much during evaporation that the structure is broken. This is why aerogels cannot be produced by air drying, nor by drying in the oven, because the same thing happens there.

What are capillary forces?

Capillaries are fine, long cavities, i.e. narrow tubes or gaps. When liquids come into contact with a capillary, the attractive forces between the liquid and the capillary wall are often greater than the attractive forces within the liquid, namely when the liquid wets the material. Capillary forces then act at the boundary between the liquid, wall and air, causing the liquid in the capillary to rise against gravity. In wide vessels, these forces at the edge do not play a major role, but they do in narrow capillaries. Capillary forces, for example, cause liquid wax in the wick to rise to the flame and porous materials such as bricks, textiles and paper to soak up water. Similarly, when blood is drawn from a finger, the blood is drawn up a thin glass capillary.

Capillary forces also occur when liquids evaporate in narrow cavities, namely when the water has already evaporated at the exit of the pore, but the pore "holds" the liquid due to the capillary forces. A so-called "meniscus", a curved surface, is formed, see Fig. 3.

The narrower a tube or pore is, the greater the curvature and the greater the capillary force! As the pores in gels are extremely small, very strong capillary forces occur when liquids evaporate in these pores. However, as these forces act in the interior of the pores, they pull the walls of the pore together and the pore is destroyed as the walls collapse (see Fig. 4).



Figure 4: Grapes and raisins:
an example of fruit shrinking during drying.

We can observe this effect when we dry a hydrogel slowly in the air (or faster in the oven), but also when fruit and vegetables are dried in the oven. They shrink and shrink, because the pores in them are destroyed by the capillary forces.

Sounds complicated? There is a simple summary on the reverse side of this page 😊



Figure 1¹: Hydrogel before and after "normal" drying

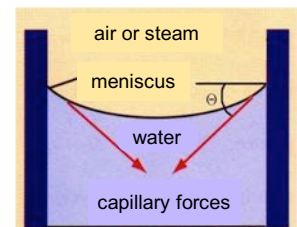


Figure 2²: Capillary forces in a pore

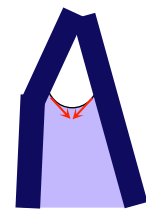


Figure 3: The capillaries are pulled together by the capillary forces and break.

Figure sources:

¹Pakowski, Z. Drying of Nanoporous and Nanostructured Materials. In Proceedings of the 14th International Drying Symposium (IDS2004), Sao Paulo, Brazil, Vol. A; 2004; pp 69–88.

²Smirnova, I. Synthesis of Silica Aerogels and Their Application as a Drug Delivery System. PhD thesis, Berlin, 2002.

**Summarized answer to the question:
Can we produce aerogels by air drying?**

- Aerogels cannot be produced by air drying, because when the water in the pores evaporates, strong forces occur at the boundary between the gas and liquid phase, which act inside the pore and contract it → "capillary forces".
- The smaller the pore, the greater the capillary forces.
- The occurrence of capillary forces must therefore be prevented at all costs during aerogel production! For this purpose, "supercritical drying" is used, which is explained in Excursus 5.
- In supercritical drying, capillary forces are bypassed as the simultaneous occurrence of liquid and gas phases is avoided. In the supercritical state namely gas and liquid phase into a single supercritical phase. This means that during supercritical drying, there is only one change without a phase transition between the liquid phase and the supercritical state and later between the supercritical state and the gas phase.

Basic Knowledge 2: Production of Aerogels

Raw materials for aerogels

Aerogels can be produced from many solid materials (even metals!). At the Institute of Thermal Process Engineering at the Hamburg University of Technology (TUHH), aerogels in particular are produced from renewable raw materials, so-called **biopolymers**.

How is an aerogel produced?

Several process steps are necessary for aerogel production, which lead from the **hydrogel** via the **alcohol gel** (**alcogel**) to the final product **aerogel**:

- 1) **Gelation:** A liquid in which a solid is dissolved gels. The product is a **Hydrogel**.
- 2) **Solvent exchange:** Water in the pores is replaced by alcohol. The product is an **Alcogel**.
- 3) **Supercritical Drying:** Alcohol in the pores is replaced by air. The product is an **Aerogel**.

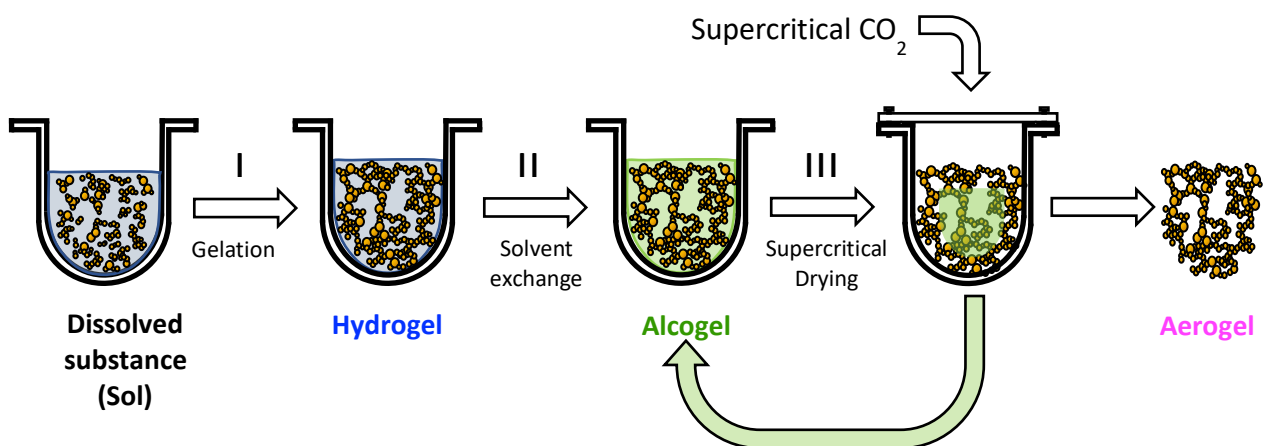


Figure 1: Aerogel production, source: TUHH, Institute for Thermal Process Engineering

As each intermediate step is important for aerogel production, we will describe each one individually and in detail below.

I. Gelation

In the first step, a hydrogel is produced (see Figure 1). During gelation, smaller building blocks cross-link to form longer chains, as can be seen in Figure 2. The cavities between these chains are the pores formed, which are filled with water. The more cross-linked chains form in the liquid, the more viscous it becomes, until finally a solid gel is obtained. This can be observed, for example, when jello powder is heated with water and then cooled again. The same happens when cooking jam or Jello. Gelation in the production process of **aerogels** behaves in a similar way. This gelation is caused either by heating, by changing the pH value or by adding

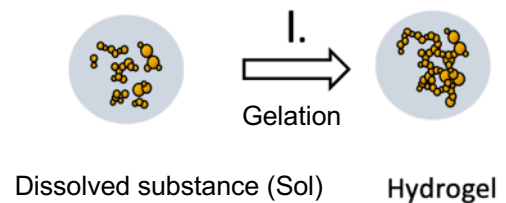


Figure 2: Gelation

Source: TUHH, Institute for Thermal Process Engineering



Figure 3: Hydrogels in bead form
 Source: <https://commons.wikimedia.org/wiki/File:SilicaGel.jpg>
 License: [CC BY-SA 2.5](https://creativecommons.org/licenses/by-sa/2.5/)

metal ions (e.g. calcium ions). The Jello can be mixed in a large or small bowl. Hydrogels can also be molded into different shapes. However, for consistent properties and short drying times, it has proven to be best to produce only small particles, as shown in Figure 3. These are produced, for example, by dropping the sol (the dissolved substance) into a solution containing a cross-linking agent. This is also used in the video in the Kniffelix.de Aerogel Mission 2e, which you can access with the QR code „Video gelation“.



Video gelation

This first step is a chemical reaction, which is why it is of particular interest to chemists. The following steps are more the responsibility of chemical and process engineers.

II. Solvent replacement

The second step is a preparatory step for the subsequent drying process: the hydrogel is converted into an alcogel by replacing the water in the pores with alcohol (chemical name: ethanol). To do this, the gels are placed in ethanol. The water now gradually migrates (diffuses) out of the pores of the gel, while the ethanol penetrates the pores. Ethanol and water mix in the process. This liquid must therefore be poured off several times and replaced with fresh ethanol until the gel has an ethanol content of 97% or higher. This is important for the subsequent drying process. The hydrogels usually become firmer and less wobbly on their way to becoming an alcogels, sometimes they also shrink a little.

Why do you need to replace the solvent?



Solvent
exchange

To put it simply: because alcohol has a lower boiling point than water. It is therefore easier to get out of the pores in the next step and under gentler conditions than water. - However, it is not quite that simple. We need to know a little more about aggregate states of matter, phase diagrams and miscibility of substances. You will find explanations to these topics in the excursuses "Solvent exchange" and "Supercritical drying", which you can access on www.kniffelix.de via the shown QR codes.



Supercritical
drying

III. Supercritical drying



Figure 4: Hydrogel (left) and shrunken hydrogel after air drying (right)
 Source: Pakowski, Z. Drying of Nanoporous and Nanostructured Materials. In Proceedings of the 14th International Drying Symposium (IDS2004), Sao Paulo, Brazil, Vol. A; 2004; pp 69–88.

To turn the alcogel into an aerogel, the liquid it contains must be removed, i.e. the gel must be dried. However, this must be a special drying process, because if the alcogel or hydrogel were left to stand in the air or dried in an oven, the liquid in it would evaporate or vaporize and the gel would shrink, see Fig. 4. This is due to the capillary forces that occur when the liquid withdraws from the pores at the boundary between the liquid, the pore wall and the gas phase. These forces cause the liquid to cling to the pores, see excursus "Capillary forces" on www.kniffelix.de with the adjacent QR code. **To avoid shrinkage due to capillary forces, the gel must not "notice" that the liquid is being replaced by gas.**



Capillary forces

Therefore, drying must not result in a state in which a gas and a liquid phase are present at the same time. This is avoided by drying with supercritical carbon dioxide at 31°C (304 K) and 74 bar in a high-pressure container (a so-called autoclave). You know carbon dioxide in its gaseous form as a component of air. However, it can be liquefied under pressure and used as a solvent. If it is also heated above 31°C, it enters the supercritical state, where there is no difference between the gas and liquid phases. This is how supercritical drying takes place, as shown by the red arrow added in Figure 5.

To do this, the **alcogel** is placed in the autoclave. The container is then pressurized and heated until the supercritical state of carbon dioxide is reached and the contents are rinsed with supercritical carbon dioxide for hours until the ethanol has been almost completely rinsed out. The pressure is then lowered so that supercritical carbon dioxide becomes gaseous carbon dioxide again. This produces an **aerogel** whose pores initially contain gaseous carbon dioxide instead of solvents, which is gradually replaced by air after removal from the autoclave.

As the pores and the shape of the gel are retained during supercritical drying, the gel does not shrink, so the volume remains the same, see Figure 6. At the same time, however, the weight is reduced, as air is much lighter than the liquid that was previously in the pores. Dry **aerogels** are therefore extremely light and have a very low **density**.

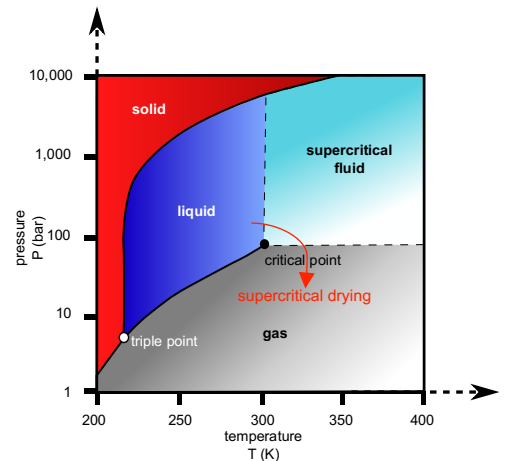
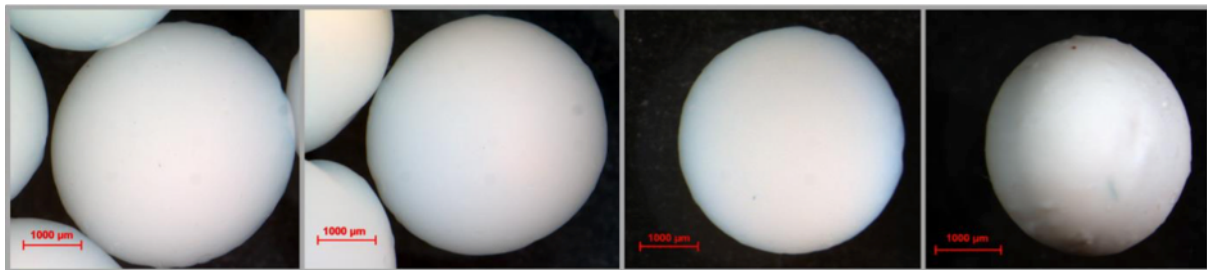


Figure 5: Carbon dioxide pressure-temperature phase diagram

Source: By Ben Finney / Mark Jacobs - Commons, Carbon dioxide pressure-temperature phase diagram.jpg, CC0,

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Fresh balls in sodium hydroxide solution

Hydrogel

Alcogel

Aerogel

Figure 6: Particle on its way to becoming an **aerogel**, after the respective production steps. The volume barely changes.

Source: TUHH, Institute for Thermal Process Engineering

Excursus 2:

Raw Materials for Aerogels - Example Biopolymers

Aerogels can be produced from gelling substances such as pudding, Jello as well as many plant and animal raw materials, so-called biopolymers (explanation: see next page). Some of these raw materials are presented in the table:






Name	Image	Origin and Use
Cellulose	 <p><i>Image 1: Cotton It consists of almost pure cellulose.</i></p>	<p>Cellulose is the main component of plant cell walls and therefore the most common biomolecule. Cellulose is used as a raw material in the paper industry.</p>
Alginate und Agar agar	 <p><i>Image 2: Brown algae Alginate is obtained from this.</i></p>	<p>The biopolymer alginate - also known as alginic acid - is mainly obtained from brown algae, which are either collected at low tide or harvested by divers in special boats. Alginate is used as a vegan gelling agent in the kitchen, among other things.</p> <p>More common is agar agar, which is also obtained from algae, but gels a little differently.</p>
Starch	 <p><i>Image 3: Starch</i></p>	<p>Starch is a natural biopolymer that is stored in the cells of plants in the form of starch granules as an energy storage substance. In the kitchen, corn, potato or wheat starch is used to thicken sauces, such as cake glaze, for puddings and baked goods, and as an adhesive (wallpaper glue), for example.</p>
Chitosan	 <p><i>Image 4: Crab Chitosan is extracted from the shell..</i></p>	<p>Chitosan is Greek and means shell or armor. It is obtained from chitin; the main source is the shells of shrimps and crabs. Chitosan is used, among other things, as a filter material for water treatment or in sewage treatment plants.</p>
Pectin	 <p><i>Image 5: Pectin is contained in apples, for example.</i></p>	<p>Pectins are found in the firmer parts of most plants, i.e. in stems, flowers, leaves, fruit, etc. Pectin is a good vegan alternative to gelatine as it is purely plant-based. It is mainly used when making jam.</p>

Image sources:

Image 1: by Philmarin, <https://de.wikipedia.org/wiki/Cellulose#/media/Datei:Alg-frut-6.jpg> License: [CC BY-SA 3.0](https://creativecommons.org/licenses/by-sa/3.0/)

Image 2: by Stemonitis, https://de.wikipedia.org/wiki/Braunalgen#/media/Datei:Fucus_serratus2.jpg License: [CC BY-SA 2.5](https://creativecommons.org/licenses/by-sa/2.5/)

Image 3: by Picasa author Kalaya, <https://commons.wikimedia.org/w/index.php?curid=9939132> License: [CC BY-SA 3.0](https://creativecommons.org/licenses/by-sa/3.0/)

Images 4 and 5: own images

Explanation: Biopolymers

To understand what **biopolymers** are, you first need to know what polymers are. Polymers are chemical compounds that consist of chain or branched molecules (so-called macromolecules). Chemists probably think of plastics first, but nature also has many polymers to offer. Biopolymers are a subgroup of polymers. They are mostly of natural origin, but industrially produced polymers can also be described as biopolymers if they are biodegradable, i.e. if they return to the biological cycle.

Biopolymers are sustainable and environmentally friendly due to their production based on renewable raw materials and/or their biodegradability. In addition, some of them occur in large quantities as residual materials that arise during the processing of food, wood, animals, etc., which would otherwise have to be disposed of as waste. It therefore makes sense to develop ideas on how to obtain valuable products from these residual materials. This idea of the circular economy also makes biopolymers particularly interesting for aerogel production!

Excursus 3: Hydrogel formation

On the example of alginate gelation ("egg-box model")

Aerogels can be made from sodium alginate, for example, a vegetable gelling agent from brown algae. This requires sodium alginate and calcium chloride. This can be used to produce a hydrogel using simple household appliances. The experiment instructions can be accessed using the adjacent QR code. The gelling of the alginate can also be seen in the gelation video on aerogels.kniffelix.de (→ QR-Codes on right).

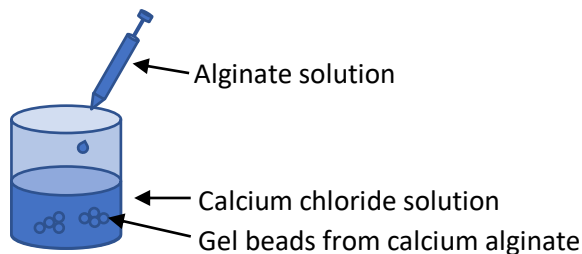


Experiment
instructions



Video gelation

First, the alginate and calcium chloride are dissolved in water in separate containers. The alginate solution is then dripped into the calcium chloride solution using a syringe or pipette. This forms solid gel beads.



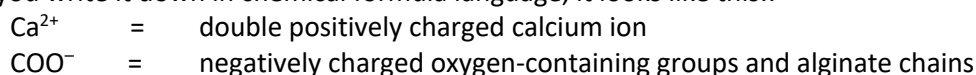
The gelation mechanism in the process is referred to as the "egg-box model".

What is the "egg-box model"?

The "egg-box model" mechanism is when alginate chains meet calcium ions. The alginate chains arrange themselves in such a way that they enclose the calcium like an egg in an egg carton - hence the name "egg-box model"

This enclosing happens because chemical groups with different charges attract and link each other. You probably know this in everyday life from magnets, where the north and south poles attract each other. This is exactly what happens between the calcium ions and the alginate chains, or more precisely with the oxygen atoms in the alginate chains: some oxygen atoms carry a negative electrical charge, while the calcium ions are positively charged. This is why they attract each other and bond.

If you write it down in chemical formula language, it looks like this::



Each double positively charged calcium ion can link two alginate chains together, because the calcium ion bonds with two singly negatively charged COO^- groups.

In the diagram you can see what it looks like in chemical formula language when alginate chains and calcium ions combine.

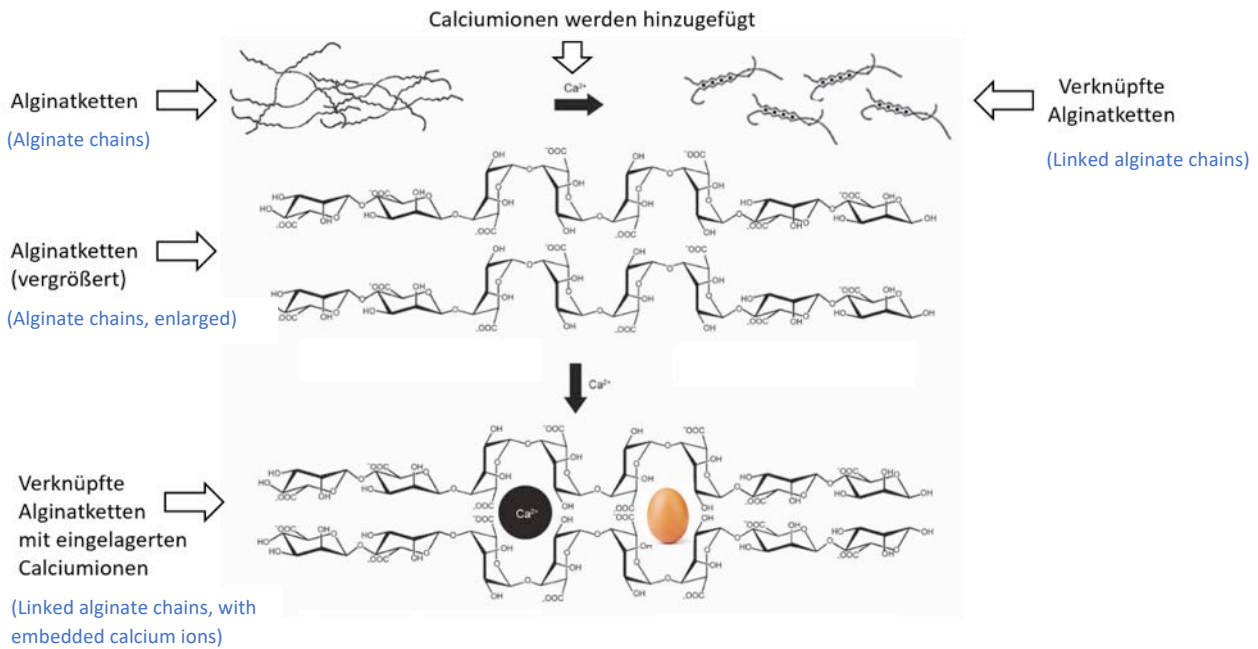


Image source: <https://doi.org/10.3144/expresspolymlett.2017.26> with added translation

When it comes to gel formation, you have to imagine that this reaction occurs very frequently in every alginate chain.

This creates a linked alginate chain network with pores, the "alginate hydrogel".



Image 1: Alginate hydrogel

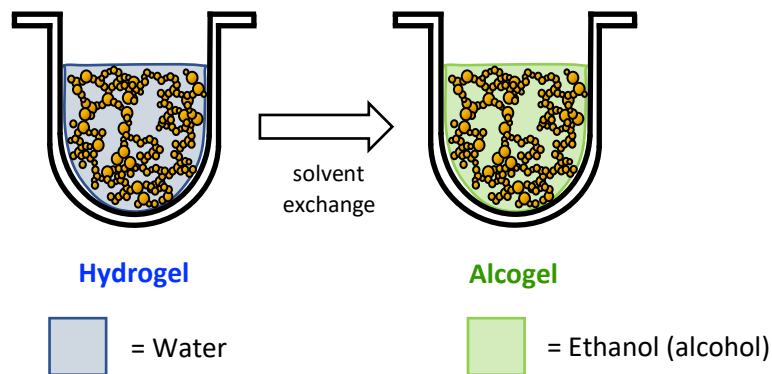
Source: TUHH, Institute for Thermal Process Engineering

You can also make an artificial egg with alginate, orange dye and wax. Watch this fun video on YouTube: <https://www.youtube.com/watch?v=e8KibU9Ykvc>

Excursus 4: Solvent Exchange

What is a solvent? Solvents are chemical compounds that (dissolve) other substances without a chemical reaction occurring between the two. Solvents are usually liquids, such as water or alcohol. For example, water is a good solvent for common salt.

When exchanging a solvent, one solvent is logically replaced by another.



In the production of aerogels, we replace the water in the pores of the hydrogel with the alcohol ethanol. The result is an alcogel. The ethanol is then replaced by another solvent, so-called "supercritical carbon dioxide", as this is the only way to maintain the structure during drying.

But why is the solvent exchange needed at all and why is the water in the pores replaced by ethanol?

The reason for this is that the liquid must be removed without a phase change between liquid and gas taking place. This is why the supercritical state is used, in which the liquid and gas phases are one, see Excursus 5. This state of matter, which is rarely mentioned in school, occurs at high temperatures and pressures, the values of which, like the boiling temperature, differ from substance to substance.

Table 1: Temperatures and pressures that must be exceeded for the supercritical state

Substance	Temperature	Pressure
Water	374,12 °C	220,9 bar
Ethanol	240,75 °C	61,5 bar
Carbon dioxide	30,98 °C	73,8 bar

Table 1 shows the values for water, ethanol and carbon dioxide. It can be seen that extremely high pressures and temperatures are required for water in order to reach the supercritical state. On the one hand, this could damage the structure and, on the other hand, would result in high production costs. These conditions are better with ethanol, but even better with carbon dioxide, which is why it is used for supercritical drying. However, switching directly from water to carbon dioxide would be problematic, as water and carbon dioxide do not mix well. Ethanol is therefore a good intermediate step.

Excursus 5:

Supercritical drying explained using the phase diagram

As you probably know, there are three different states of matter: solid, liquid and gas. For example, water is referred to as ice, water or steam (water vapor) depending on its state of aggregation. What is often not mentioned at school is that there is also a **supercritical state**. But how can we even imagine it?

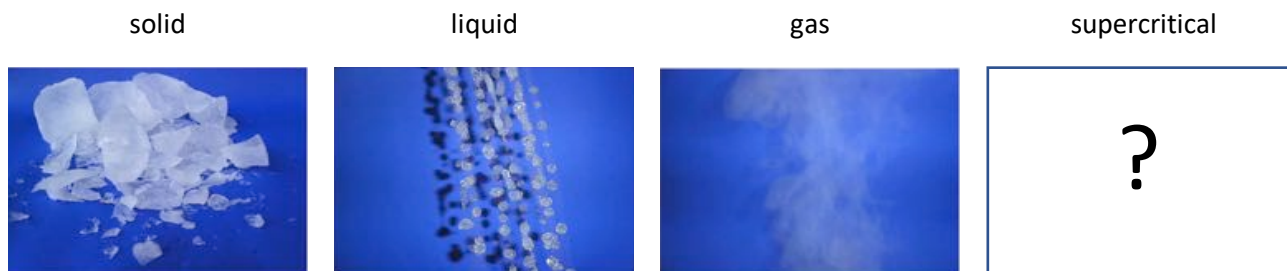


Figure 1: States of aggregation

Source: <https://de.serlo.org/chemie/25371/aggregatzustand>, License CC-BY-SA4.0

Let's take a closer look at this first: The physical state of a substance depends on the temperature and pressure, which is why substances can change their physical state when the temperature or pressure changes. Simple examples are the freezing of water in the freezer or evaporation in a pot when heated. In each case, the temperature is changed to bring about the change in the state of matter. But pressure also has an influence: you may know that the fact that water boils at 100° C only applies at normal pressure. In a pressure cooker, you can increase the pressure so that the water only starts to boil at a higher temperature, e.g. 120°C. The higher temperature means that the food does not take as long to cook, which saves time and energy. If you want to cook on a high mountain instead, where the air pressure is lower, the water boils at a lower temperature. Food therefore takes longer to cook.

The phase diagram

Since the state of aggregation depends on temperature and pressure, the transition between two states of aggregation also depends on temperature and pressure. There is not just a boiling temperature or a boiling point, but a **vaporization curve**, with the boiling temperature as a function of pressure.

In a phase diagram (see figure 2 on the right), the states of aggregation can be shown as a function of pressure and temperature with curves representing transitions between the phases.

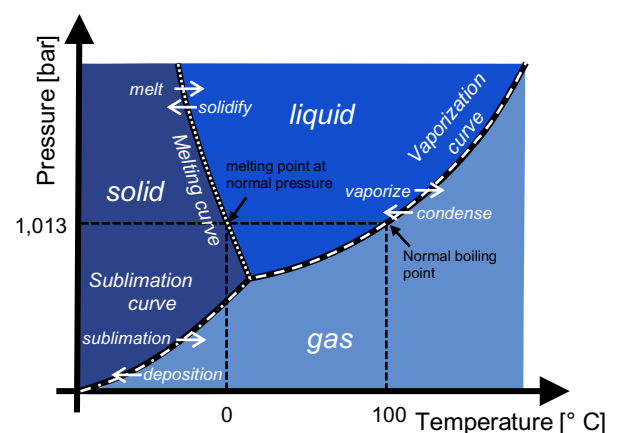


Figure 2: Phase diagram of water

The influence of temperature and pressure explained in the particle model

The states of matter can be visualized in the **particle model**: In the **solid state**, the particles are close together and can hardly move. They are usually depicted as single-colored spheres, but since attractive forces between the particles also play a role, here they are shown in red and green like magnets (different colors attract each other, the same colors repel each other). When a solid is heated, the particles move slightly more, so the solid expands. At the same time, the forces of attraction become weaker due to the greater distance. (Exception: water between 0 and 4°C expands during cooling → density anomaly of water)

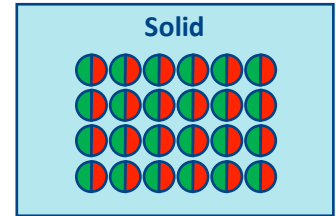


Figure 3: Solid in the particle model

When the melting point is reached during heating, more and more particles are released from the tight solid arrangement and enter the **liquid state**. There they are no longer in a fixed position but can move around. As a result, liquids no longer have a solid form, but still have a defined volume. If the liquid is then heated further, the same applies as in the solid phase: more energy is added to the particles so that they move more. The distance increases, the attractive forces decrease and the liquid expands.

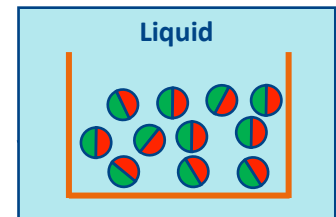


Figure 4: Liquid in the particle model

Through further heating, a threshold value is also reached at some point: the boiling point. At this point, more and more particles are released from the attractive forces still acting in the liquid phase and move freely in space as individual particles. This puts them in the **gaseous state**, where they have the most distance between them and move very quickly. (An accidental collision of such particles is more likely to lead to a rebound due to the high speed than to the forces of attraction coming into play again).

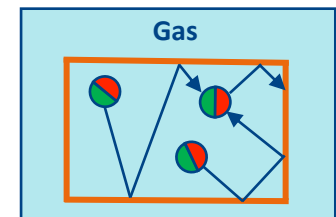


Figure 5: Gas in the particle model

Up to this point, the influence of temperature on the aggregate state has been described.

But what influence does pressure have? If you increase the pressure, you lock the same number of particles into a smaller volume. They then come closer together again. This is particularly easy when the particles are in the gas phase. They can then be easily pressed together. In the liquid and especially the solid phase, high pressure must be applied to press the particles even closer together.

If you visualize that the hotter a liquid is, the more the particles move, and at the same time that the higher the pressure, the more particles a volume contains, you can perhaps imagine that the difference between the gas and liquid phases disappears when high temperatures and high pressures are present at the same time. At this point, the **supercritical state** is reached.

IMPORTANT: In the supercritical state, there is no difference between the gas and liquid phases. It is achieved at high temperatures and pressures. Exactly how high these are depends on the substance.

Can you see the supercritical state?

We cannot provide a supplementary image for the first page of this explanation, but researchers can observe in experiments when the critical point is reached: to do this, they use a viewing chamber, a pressure-resistant heatable container with a window and fill it with water, for example, and bring it to boiling. At the boiling point, they see a liquid and a gaseous phase, which are separated by a phase boundary.

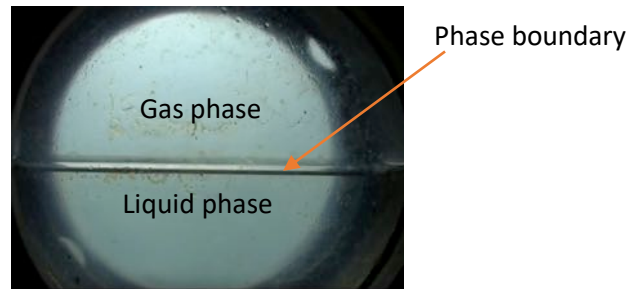


Figure 6: Viewing chamber with two phases and a clearly visible phase boundary

If you now change the pressure and temperature at the same time so that you remain on the boiling curve, you will eventually reach the critical point at which the difference between the gas and liquid phases disappears. There you will no longer see a phase boundary. **The disappearance of this line is therefore the only thing you can see.**

Let's compare the supercritical state of water, ethanol and carbon dioxide in the phase diagram:

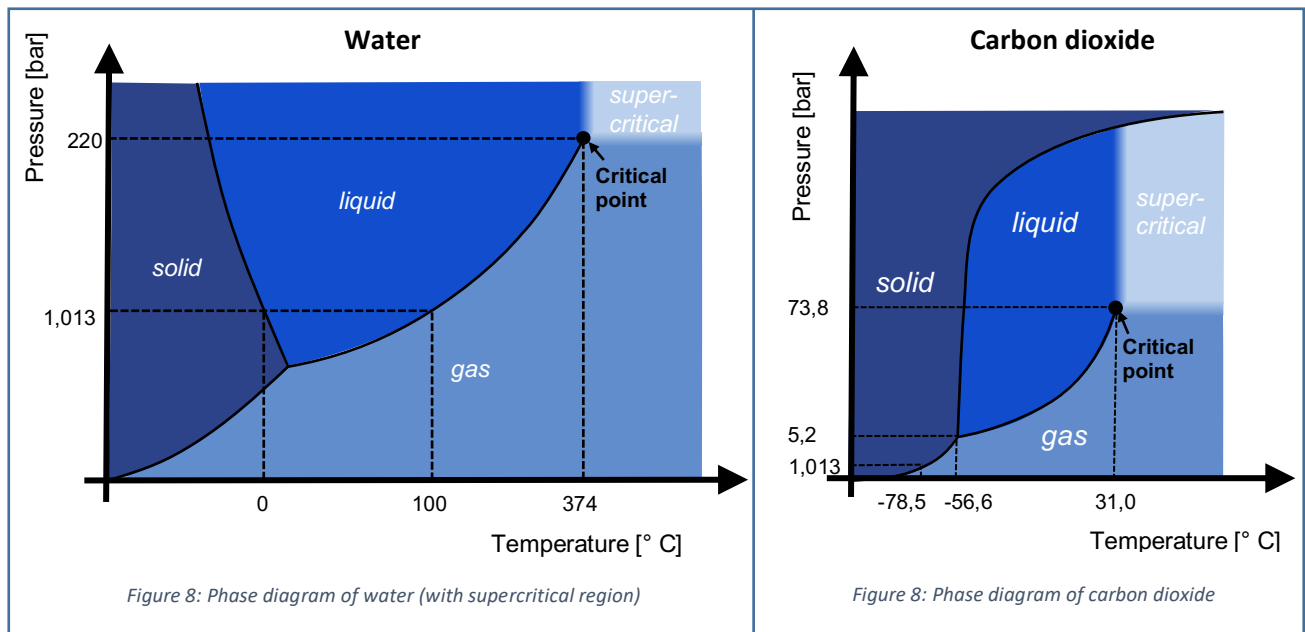


Figure 8: Phase diagram of water (with supercritical region)

Figure 8: Phase diagram of carbon dioxide

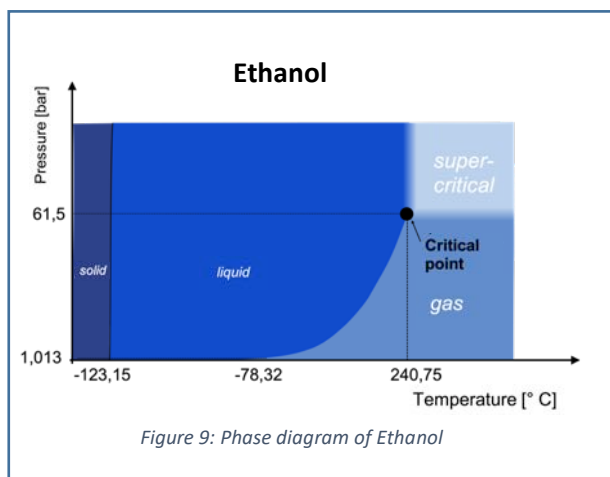


Figure 9: Phase diagram of Ethanol

In the phase diagram, the critical point is the upper end of the boiling curve. The supercritical state begins above this point.

To achieve the supercritical state of water, a very high pressure of 220 bar and a high temperature of 374 °C are required. The values are lower for many other substances, e.g. only 61.5 bar and 240 °C are required for ethanol and only 73.8 bar and as low as 31 °C for carbon dioxide.

Basic Knowledge 3: Structure, Properties and Applications of aerogels

The special thing about all aerogels is their structure: Like sponges, they contain many pores, but their pores are much smaller so that they are not visible to the naked eye. Therefore, they can only be observed with high-resolution microscopes (e.g. scanning electron microscopes). A typical pore structure of an aerogel made from the biopolymer alginate is shown in Figure 1.

Because aerogels have so many pores, they not only have an outer surface, but above all a huge inner surface. If you could unfold a few grams of an aerogel and spread out the surface area of all the pores, it would be about the size of a soccer field!

Although the pores in aerogels are very small, they are larger than the pores in activated carbon, for example. This means that substances can easily get into (and out of) the pores, which is useful for many applications. This makes aerogels interesting, for example, as catalyst carriers or as carriers for medicines and flavorings. You can find out even more about pores in Excursus 6: Interesting facts about pores.

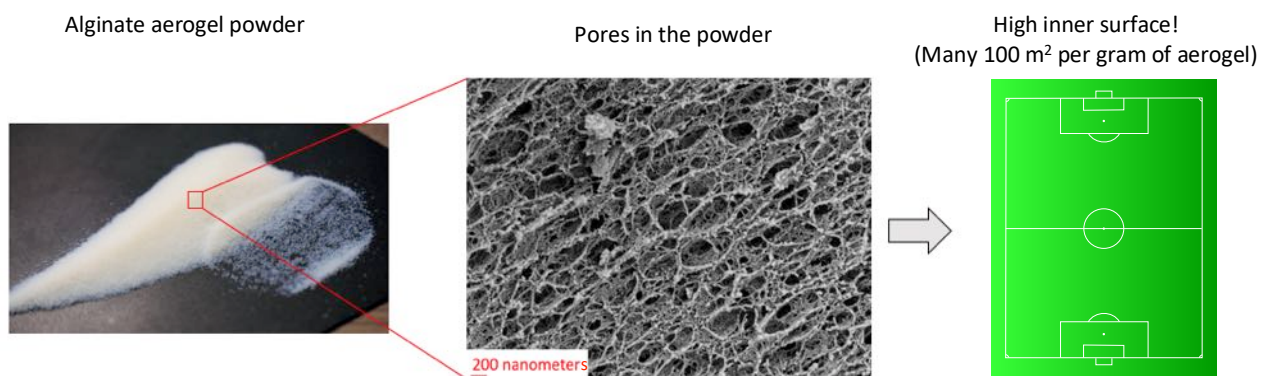
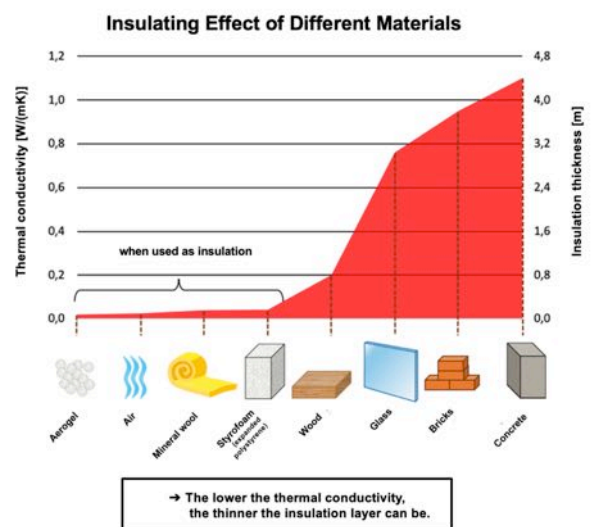


Figure 1: Aerogels are characterized by a high inner surface area

The special properties of aerogels are summarized below:

- High pore volume (consist of up to 99% air)
- "Ultralight" (density of 0.01 g/cm^3 achievable. For comparison: water 1 g/cm^3 , air 0.001 g/cm^3 , Styrofoam $0.02 - 0.06 \text{ g/cm}^3$)
- Extremely high internal surface area due to the small pores
- High thermal insulation and soundproofing: As heat and sound are "trapped" in the pores, they can only penetrate aerogels with difficulty.

These properties give rise to many possible applications for aerogels, which also depend on the raw material from which the aerogels are made. Applications are listed on the reverse.



What are the special properties of biopolymer aerogels? What are they used for?

Like all aerogels, biopolymer aerogels have extremely low thermal conductivity. They can therefore be used as super-insulation materials, for example in the automotive industry and in insulation systems for buildings. They are also suitable for material separation, e.g. for oil-water separation. Depending on the type, the aerogel only binds the oil and not the water or vice versa.

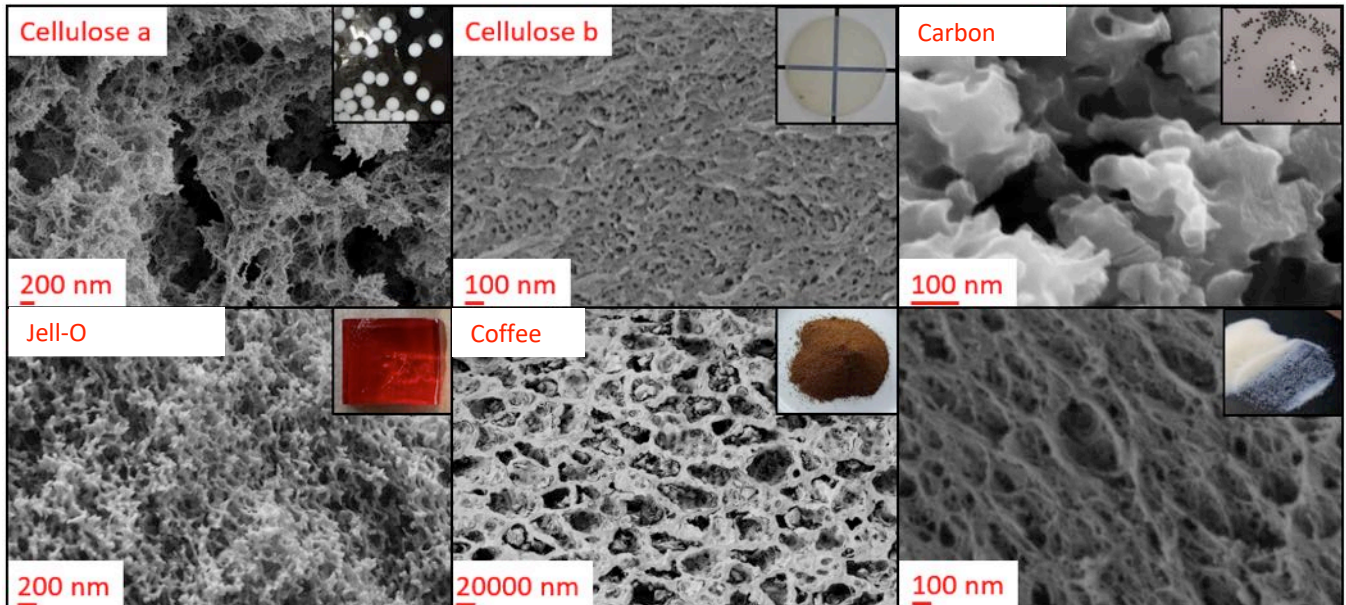
Even though biopolymer aerogels are still hardly widespread, there is great potential for new applications. For a long time, they could only be produced in small quantities in the laboratory, but with the EU research project NanoHybrids, it was possible to further develop the manufacturing process so that larger quantities could be produced for the first time. This research project was carried out from 2015 to 2019 by twelve research institutes and industrial partners from seven countries under the leadership of Prof. Smirnova from the Institute of Thermal Process Engineering at the Hamburg University of Technology.

If more biopolymer aerogels are now available and manufacturing costs fall, their use in various areas is conceivable. In addition to heat-insulating and substance-separating properties, the high inner surface area to which substances can be bound or released from plays a particularly important role. Using proteins and starch as starting materials, edible aerogels can be produced which could be used in the medical and food sectors: for example, medicines could be incorporated into aerogels which could gradually be released in the body. Aerogels could also be used as carriers of flavorings and vitamins for food supplements or active ingredients in cosmetics. In agriculture, they could release pesticides in a controlled manner and thus lead to a more economical use of these products.

Overview of aerogel applications:



Excursus 6: Interesting Facts About Pores



Aerogels can have very different properties: Some aerogels are very good heat insulators, for example, while others are particularly suitable as adsorbers (i.e. for binding substances to their surface).

The properties of an aerogel primarily depend on the size of the pores in the aerogel: Cellulose aerogels can be either transparent or opaque depending on the pore size. Aerogel researchers are therefore constantly trying to obtain the most suitable pores for the application the aerogel is intended for. So-called "mesopores" are normally suitable: These are so tiny that we cannot see them with the naked eye!

Their diameter ranges from 5 - 50 nanometers: this is particularly small, as a million nanometers fit into one millimeter. This is why special scanning electron microscopes are needed to see the pores at all.

Unit	Symbol	Conversion
Millimeter	mm	
Micrometer	μm	$1 \mu\text{m} = \frac{1}{1.000} \text{ mm}$
Nanometer	nm	$1 \text{ nm} = \frac{1}{1000} \mu\text{m} = \frac{1}{1.000.000} \text{ mm}$

Task:

Above you can see microscopy images of various aerogel pores. In each picture you will find the following information:

- 1) The material
- 2) What the aerogel looks like
- 3) a scale in nanometers (nm).

As you can see, the pores are different sizes and have different shapes. Try to arrange the pictures in an order: Which one do you think is the "best" aerogel? Remember: Aerogel researchers want to have only mesopores in their aerogel and no larger pores or gaps. The more fine pores there are, the better.



Excursus 7: Study Orientation in the Field of Aerogels

What tasks are there in (aerogel) research and which degree programs are of interest??

Chemistry:

As you have already noticed, the production of an aerogel requires knowledge from various fields. In addition to chemistry, this includes not only mathematics but also physics and biology. In the first step, the production of hydrogels is determined by the interactions of the polymers with each other and with the gelling agent. By varying these two components and their properties, the viscosity of the gel and thus also the structure of the aerogel after drying is influenced. If you are particularly interested in this step, studying **chemistry** could be something for you.

Chemical Engineering & Mechanical Engineering:

If you are more interested in the interaction of technology with chemical and physical processes, a degree in chemical engineering could be the right choice for you. This course of study deals, for example, with the influence of the autoclave on the finished aerogel (e.g. through pressure or temperature) or how the production process can be optimized (low energy and material consumption). The development and design of suitable systems (e.g. the autoclave) and how they work are part of a **chemical engineering** or **mechanical engineering** degree course.

Modeling:

One topic that is becoming increasingly interesting these days is virtual models. With the help of such a model, the required process conditions (e.g. pressure and temperature) and properties of the finished aerogels can ideally be predicted without having to carry out experiments in the laboratory. This saves researchers a lot of work, costs and time. Modeling is another field that can be studied in **chemical engineering**. This usually involves working on computers and using modeling programs or even writing models yourself in different programming languages. Programming skills are therefore an advantage here.

Even as a student, you can work as a student assistant in research, e.g. carrying out and evaluating experiments. The Bachelor's degree can be followed by a Master's degree and then a doctorate. During this time, you are employed as a research assistant and work on research projects or parts of them largely independently. At the same time, you often also work in teaching. A further step on the career ladder at university is the habilitation, which is a prerequisite for a professorship. In interviews on the website www.kniffelix.de you can get to know aerogel researchers working at different levels and doing various tasks.

For "Interviews with aerogel researchers" see <https://kniffelix.rz.tu-harburg.de/begib-dich-auf-spurensuche/projektuebersicht/aerogel-mission/exkurs-interviews-mit-aerogel-forschern/>

You can opt for English or German subtitles if you wish.