The Weird and Wonderful Properties of Water

Key Stage 4 Programme – 2016-2017

Teacher Name Dr M Stewart

Pupil Name_____

Fill this in with your teacher.

Timetable – Tutorials

Tutorial	Date	Time	Location
1a		12:25pm-12:55pm	
1b		12:25pm-12:55pm	
2a		12:25pm-12:55pm	
2b		12:25pm-12:55pm	
3a		12:25pm-12:55pm	
3b		12:25pm-12:55pm	
4a		12:25pm-12:55pm	
4b		12:25pm-12:55pm	
5a		12:25pm-12:55pm	
5b		12:25pm-12:55pm	
6a		12:25pm-12:55pm	
6b		12:25pm-12:55pm	

Timetable – Homework Assignments

Homework Assignment	Description	Due Date
Tutorial 1	Baseline Test	
Tutorial 2	Specific Heat & Capillary Action Calculations	
Tutorial 3	Prepare Presentation	
Tutorial 4	Draft Assignment	
Tutorial 5	Final Assignment	

Assignment Submission – Lateness and Plagiarism

Lateness	
Submission after 4.00pm on	10 marks deducted
Plagiarism	
Some plagiarism	10 marks deducted
Moderate plagiarism	20 marks deducted
Extreme plagiarism	Automatic fail

KS4 Programme 2016-17 – Pupil Feedback Report

Grade	Marks	What this means
1st	70+	Performing to an excellent standard at A-Level
2:1	60-69	Performing to a good standard at A-Level
2:2	50-59	Performing to an excellent standard at current key stage
3rd	40-49	Performing to a good standard at current key stage
Working towards a pass	0-39	Performing below a good standard at current key stage
Did not submit	DNS	No assignment received by The Brilliant Club

Lateness	
Any lateness	10 marks deducted
Plagiarism	
Some plagiarism	10 marks deducted
Moderate plagiarism	20 marks deducted
Extreme plagiarism	Automatic fail

Name of RIS Teacher			
Title of Assignment			
Name of Pupil			
Name of School			
ORIGINAL MARK / 100		**FINAL MARK / 100**	
DEDUCTED MARKS		**FINAL GRADE**	

If marks have been deducted (e.g. late submission, plagiarism) the teacher should give an explanation in this section:

Learning Feedback Comment 1 - *Enter Key Learning Priority Here*	
What you did in relation to this Key Learning Priority *Enter feedback here*	**How you could improve in the future** *Enter feedback here*
Learning Feedback Comment 2 – *Enter Key Learning Priority Here*	
What you did in relation to this Key Learning Priority *Enter feedback here*	**How you could improve in the future** *Enter feedback here*
Learning Feedback Comment 3 – *Enter Key Learning Priority Here*	
What you did in relation to this Key Learning Priority *Enter feedback here*	**How you could improve in the future** *Enter feedback here*
Resilience Comment	
How you showed learning resilience during the course *Enter feedback here*	**How you could build learning resilience in the future** *Enter feedback here*

Example

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Course Rationale

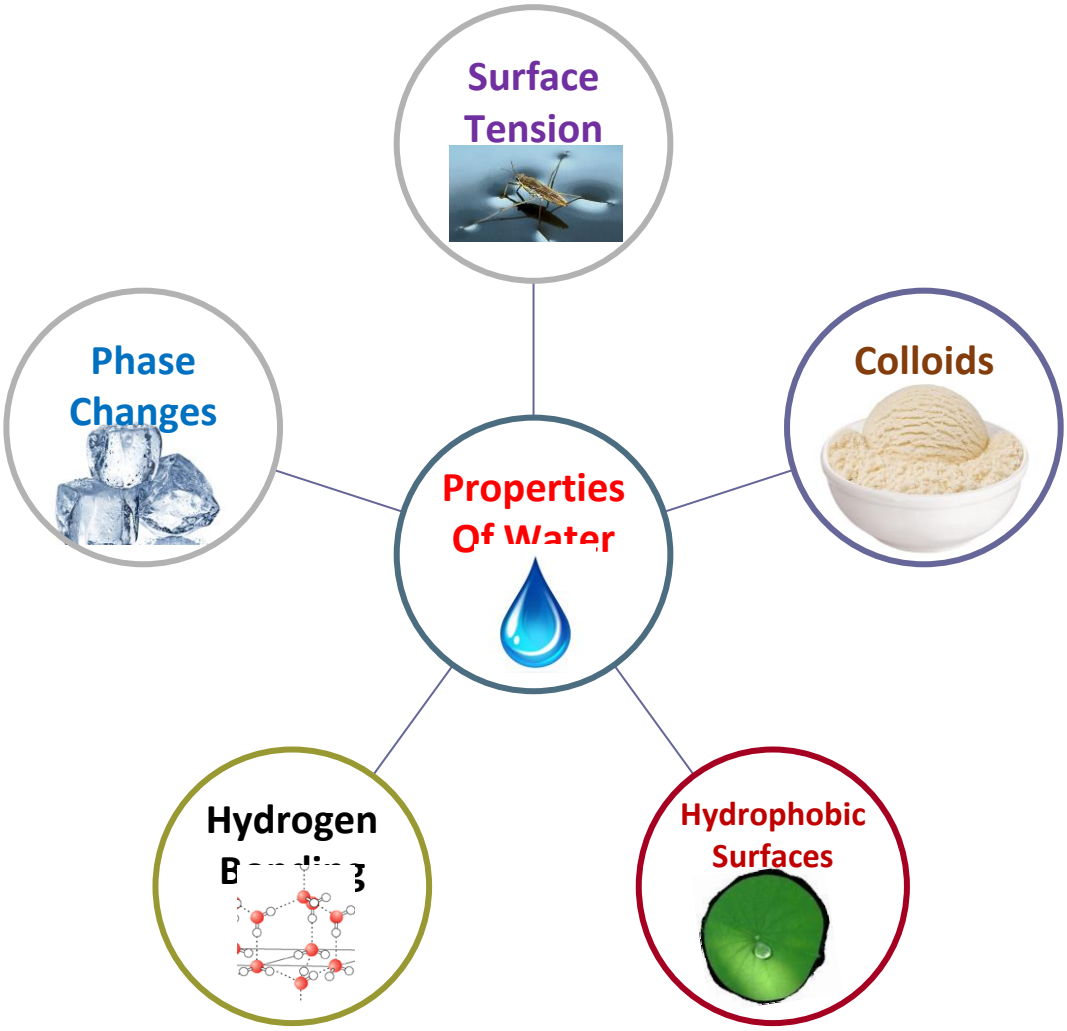
Why is there no liquid water on Mars? Why is ice slippery? Why don't the bottoms of ponds and lakes freeze in the winter? Why is Glasgow much warmer than Moscow in the winter but colder in the summer? How do insects walk on water? What is the link between lotus leaves and self-cleaning surfaces?

Water is vital to the existence of life on earth. We are so familiar with water in our everyday lives that we may think of it as very ordinary but, from a scientific view-point, its properties are highly unusual. It is the only substance that exists in all three phases (solid, liquid and gas) in nature and its extremely high surface tension allows insects to walk on water and water to be carried up through the stems of plants.

This course is aimed at students who have an interest in science. It begins with a study of phase transitions and phase diagrams (i.e., charts used to show the temperature and pressure at which different phases occur) and specifically the unusual phase diagram of water and how this relates to the bonding between water molecules. The surface tension of water is introduced in the second tutorial, and its consequences for capillary action are examined. Later in the course different surfaces, both hydrophilic ('water loving') and hydrophobic ('water fearing'), are studied. The course will also include an introduction to colloids, which have many applications in biology (e.g., blood) as well as in food science (e.g., ice cream, milk, mayonnaise, jelly). Tutorials will also include practical demonstrations.

Students will learn how to approach science problems mathematically and how to interpret graphs and phase diagrams. They will have the opportunity to make a short presentation to the group and will be encouraged to develop their scientific communication skills. In tutorial 5, a paper on super-hydrophobic surfaces will be studied as an introduction to making use of scientific literature. In the final assignment students will produce their own scientific review of a selection of the properties of water. They will be encouraged to choose the emphasis of this piece of writing according to their interests so they may choose focus either on the mathematical aspects, on experimental demonstrations or on the biological implications of the properties of water. Students will develop their scientific writing skills and will have to opportunity to demonstrate their knowledge and understanding of the topic in this extended piece of work.

Course Map


Surface Tension
Phase Changes
Colloids
Properties Of Water
Hydrogen Bonding
Hydrophobic Surfaces

Mark Scheme

Key Skill	1st	2.1	2.2
Scientific communication	☐ Writing is well structured and logical ☐ Writing is clear and precise with correct use of scientific terms ☐ Spelling, grammar and punctuation is correct ☐ References to scientific papers are included and are presented in an appropriate style ☐ Writing is relevant to the topic, interesting and holds the attention of the reader	☐ Writing is mainly well structured ☐ Writing is clear and scientific terms are mainly used correctly ☐ Most spelling, grammar and punctuation is correct ☐ An attempt is made to reference scientific papers ☐ Writing is mainly relevant to the topic and an attempt is made to engage the reader	☐ Some writing is well structured ☐ Scientific terms are used but may sometimes be incorrect ☐ Some mistakes in spelling, punctuation and grammar ☐ Limited reference to scientific papers ☐ Some writing is relevant to the topic
Numerical Analysis	☐ Calculations are clearly set-out, easy to follow and correct ☐ Mathematical Formulae are used correctly ☐ The physical implications of numerical results are explained clearly and correctly	☐ Simple calculations are clearly set-out and correct ☐ Simple Mathematical Formulae are used correctly ☐ Attempts are made to explain the physical implications of numerical results.	☐ Use of simple formula is mainly correct
Knowledge and Understanding	☐ Clear explanations and the use of relevant scientific vocabulary shows an understanding of the scientific concepts ☐ Evidence of independent research beyond the topics directly covered in the tutorials ☐ Confidently interprets and explains a phase diagram	☐ Explanations and use of scientific vocabulary shows a developing understanding of scientific concepts ☐ Independent research is attempted but may not be properly linked into the topic ☐ Understands and explains some features of a phase diagram	☐ Explanations partially correct but may show some misconceptions. ☐ Use of scientific vocabulary attempted. ☐ Limited independent research attempted. Some sources not be entirely relevant or may not be properly linked into the topic. ☐ Describes some features of a phase diagram

Glossary of Keywords

Word	Definition	In a sentence…
Phase of matter	States in which matter can exist.	There are five known phases of matter: solid, liquid, gas, plasma and Bose-Einstein condensate.
Phase diagram	A chart used to show the conditions (e.g. pressure, temperature, density) at which phases occur and coexist.	The lines on a phase diagram indicate where phase changes occur.
Phase Change	The transition from one phase to another.	Melting is the phase transition from a solid to a liquid.
Triple point	The temperature and pressure at which solid, liquid and gas coexist.	The triple point of water occurs at a temperature of 0.01^{o}C and a pressure of 0.006 atm.
Specific Heat Capacity	The amount of heat per unit mass required to raise the temperature by one degree Celsius.	Liquid water has an unusually high specific heat capacity.
Latent Heat	The energy released or absorbed during a constant temperature process, for example, a phase change.	The latent heat of fusion of a substance is the energy required to change it from a solid to a liquid at its melting temperature.
Pressure	The force per unit area that regions of solid, liquid or gas exerts on each other.	Atmospheric pressure on the surface of Mars is around 0.6% of atmospheric pressure on Earth at sea-level.
Hydrogen Bonding	A hydrogen bond is the attractive force between the hydrogen attached to an electronegative atom of one molecule and an electronegative atom of a different molecule.	The hydrogen bonds between water molecules account for many of the unusual properties of water.
Temperature	A measure of the degree of warmth of an object or substance.	The temperature of a gas increases as the average kinetic energy of its molecules increases.
Surface Tension	The elastic tendency of a fluid surface which makes it acquire the least surface area possible.	The high surface tension of liquid water allows some insects to walk on the surface.
Capillary Action	The ability of liquids to flow into narrow spaces against gravity.	Water is drawn up the stems of plants by capillary action.
Colloid	A mixture in which one substance is divided into particles and dispersed through another substance.	Milk is an example of a colloid in which small droplets of fat are dispersed in a water based solution.
Hydrophilic	Having a strong affinity with water; tending to mix with, dissolve in, or be wetted by water.	Clean glass is an example of a hydrophilic surface.
Hydrophobic Surface	Lacking affinity for water; tending to repel and not absorb water; tending not to dissolve in or mix with or be wetted by water	A lotus leaf is an example of hydrophobic surface.

Add your own words to the glossary:

Word	Definition	In a sentence…

Tutorial 1 – The tip of the iceberg

Today's Key Question(s):

- What is a phase diagram?
- How is the phase diagram for water unusual and what consequences does this have?

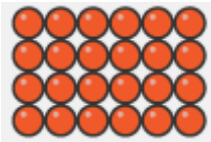
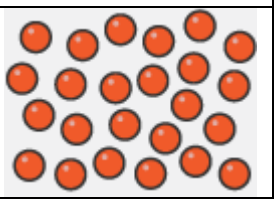
What is the Purpose of Tutorial 1?

- Recall the properties of the three main phases of matter
- Define a phase change
- Understand and use a phase diagram
- Link the unusual phase diagram for water with the hydrogen-bonding between molecules
- Explore the relevance of the phase-diagram of water for some real world examples

Today's Homework is:

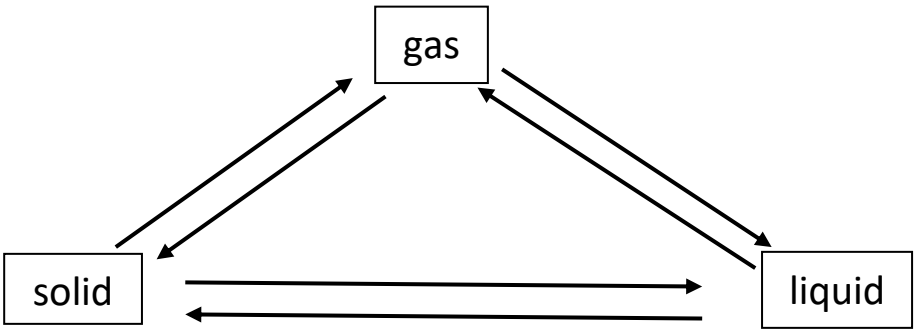
- Baseline Test

Phases of Matter (Recap)

	Solid	Liquid	Gas
Arrangement of particles			
Bonds between particles			
Shape			
Movement			
Diagram			

Phase Transitions (Recap)

Label the arrows with the names of the phase transitions



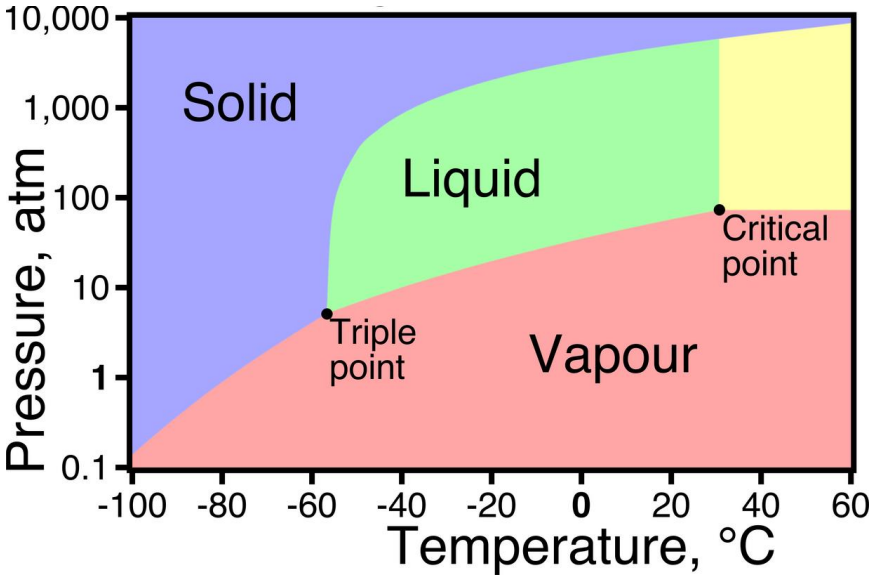
Evaporation Sublimation Deposition Condensation Melting Freezing

Hoar frost is an example of deposition

Snowflakes form in clouds by deposition

Phase Diagrams

Here is an example of a typical phase diagram (carbon dioxide)



- Make a cross on the phase diagram at room temperature (20°C) and pressure (1 atm)

- Use this cross to predict which phase of carbon dioxide is present at room temperature and pressure:

  _____

- If the temperature is fixed at 20°C and the pressure is gradually increased from 1 atm, which phase transition(s) will take place?

  _____

- Solid carbon dioxide is called dry ice. At room pressure (1 atm), which phase transition(s) will occur if dry ice heats up?

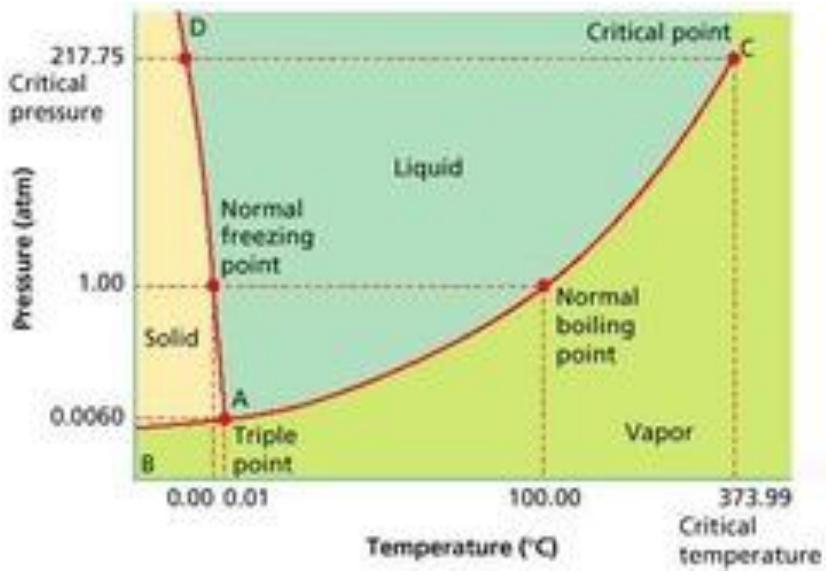
  _____

- What is the temperature and pressure at the triple point?

  _____ °C _____ atm

- Define the triple point:

  _____



- Make a mark on the phase diagram at room temperature (20°C) and pressure (1 atm). Which phase of water is present at room temperature and pressure:

  _____

- If the temperature is fixed at 0°C and the pressure is gradually increased from 0.001 atm, which phase transition(s) will take place?

  _____

- What is unusual about the phase diagram for water?

  _____

  _____

- What is strange about the density of ice?

  _____

- Atmospheric pressure on Mars is around 0.006atm. The temperature ranges from -125°C to 20°C. In what phases would you expect to find water on Mars?

  _____

  _____

  _____

Homework 1 – Baseline Test

The homework assignment for the first tutorial is a baseline test to see your initial level of attainment in this subject area. The assignment will test for some or all of the subject specific skills that are required later in the final assignment. However, it is shorter than the final assignment and is will be an introduction to the subject as well as a challenge!

Do not worry too much about doing 'well' or 'badly' on the baseline test, it takes into account the fact that you may not be familiar with the subject area. It is designed to help you and your PhD tutor identify where you are at the start of the programme and to help you measure your progress along the way.

Question 1 – Why is ice slippery?

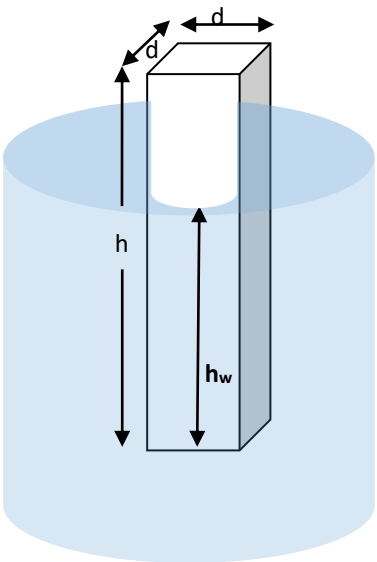
Read the first two pages of the article 'Why is ice slippery' (Rosenberg, Robert. "Why is ice slippery?" Physics Today 58.12 (2005): 50.), which can be found in Appendix 3.

Three possible reasons for ice being slippery are described on those two pages.

- Briefly summarise these three explanations, writing a short paragraph for each. Refer to the phase diagram of water where appropriate.
- Write a fourth paragraph with your conclusions: which explanation do you think is correct and why? (Or you may conclude that you do not have enough information to decide – if this is the case then explain what further information/experimental results you would require to come to a firm conclusion.)

Question 2 – The tip of an iceberg

You may have heard the expression 'the tip of an iceberg' used to refer to a situation where what you can see is only a small part of a much bigger problem. In this question you will calculate the percentage of an iceberg which is below the surface of the water.



We shall model the iceberg as a cuboid of height *h*, width *d* and depth *d*.

The height of the iceberg under the water is h_w

The density of water is 1000 kg/m^3 and the density of ice is 917 kg/m^3

Step 1

Write a formula for the mass of the iceberg (it will include *h* and *d*)

(Recall mass = density x volume)

Step 2

Archimedes principle states that for an object floating in water the mass of the object is equal to the mass of the fluid displaced.

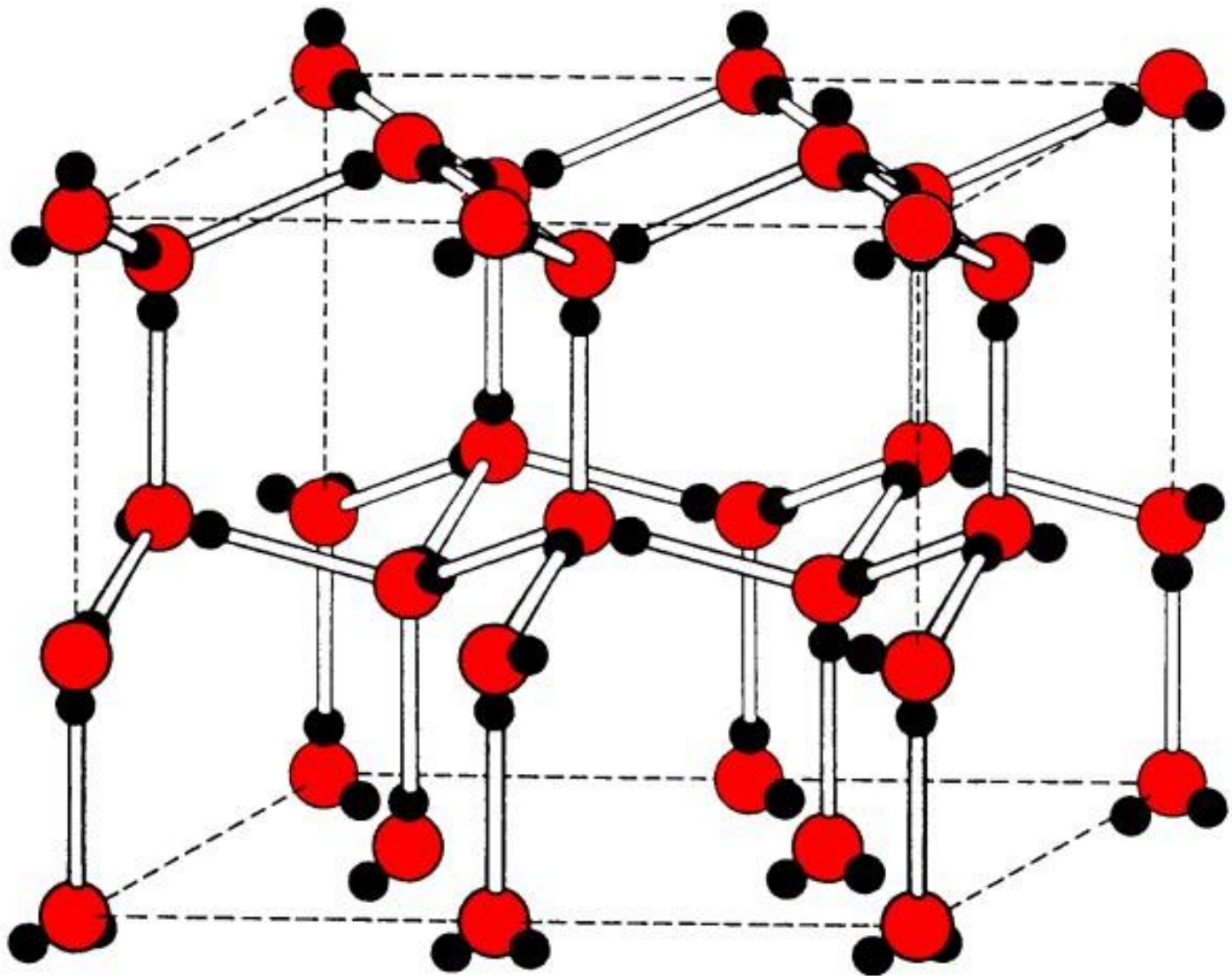
Write a formula for the mass of fluid displaced, using h_w for the height of the iceberg under water.

Step 3

Equate the mass of the iceberg (from step 1) to the mass of fluid displaced (from step 2) and rearrange this formula to find the fraction of the iceberg which is below water: $\boldsymbol{h_w / h}$

Challenge: what if the iceberg was a cylinder instead of a cuboid?

Tutorial 2 – Walking on water



Today's Key Question(s):

- What is the bonding between water molecules?
- How does the bonding between the water molecules give rise to the unusual properties of water?
- How do some insects walk on walk?
- How does water travel up through plants?

What is the Purpose of Tutorial 2?

- Hydrogen Bonding
- Specific heat capacity of water
- Surface tension of water
- Capillary action

Today's Homework is:

- Heat capacity calculation
- Capillary action calculation

Starter – Bonding Recap

- Briefly describe an ionic bond

  _____

- Briefly describe a covalent bond

  _____

- Describe the forces between **molecules** in simple covalent substances

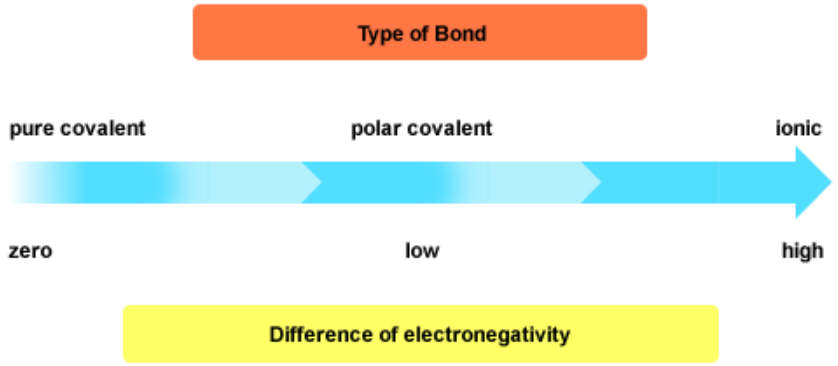
  _____

  _____

The bonds between water molecules

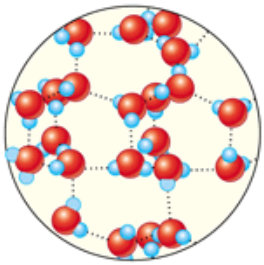
Water consists of two hydrogen atoms covalently bonding to a single oxygen atom. Draw a dot and cross diagram to show the bonding between the atoms in a molecule of water, labelling the bonding pairs and the lone pairs:

Oxygen is highly **electronegative**. This means that the oxygen atom pulls the electrons in the bonding pairs towards it. The hydrogen atoms are left 'naked' – their positive nucleus is revealed. The hydrogen is then attracted to the lone pairs of electrons on other molecules. This creates a strong **dipole-dipole interaction**, known as a **hydrogen bond**. Hydrogen bonds are much stronger than the bonds between simple covalent molecules but are weaker than the bonds between oppositely charged ions in an ionic structure.

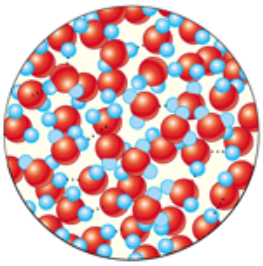


Why is ice less dense than liquid water?

The orientation of the hydrogen bonds makes the structure of ice bulky compared to liquid water:



Ice



Water

Why does is the temperature at the bottom of lakes roughly constant at around 4°C in winter, even though the air temperature may be below freezing?

How does hydrogen bonding explain the unusual melting point and boiling point of water?

Why does water have a high Specific Heat Capacity?

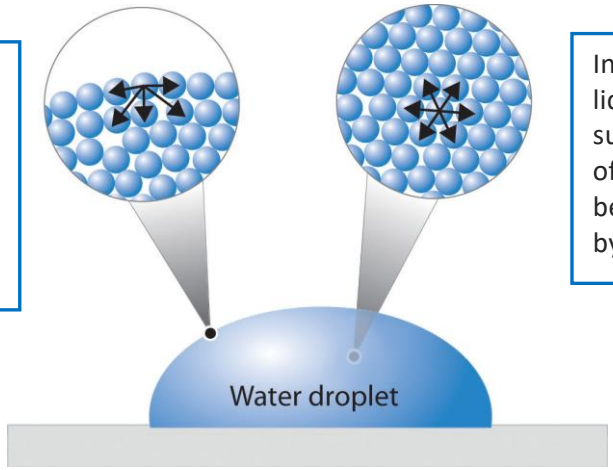
The specific heat capacity is the amount of heat needed to raise the temperature of one kilogram of a material by one degree. How do the hydrogen bonds between water molecules cause water to have a particularly high specific heat capacity? Why is the fish pleased?

The Surface Tension of Water

Surface tension is the elastic tendency of a fluid surface which makes it acquire the least surface area possible. This has the effect that the surface of a fluid acts like a thin elastic sheet.

Surface tension originates from the bonds between molecules: the molecules in the liquid are more strongly attracted to each other than they are to the air above the surface.

At the surface of the liquid the molecules are pulled down towards the rest of the liquid. This means that the molecules try to make the surface area as small as possible.



In the bulk (middle part) of a liquid the molecules are subjected to the same forces of attraction in all directions because they are surrounded by other liquid molecules.

The surface tension of water is particularly high compared to other liquids. It's those strong hydrogen bonds again!

Some consequences of the high surface tension of water:

1. Small, dense objects can float on water

2. Some insects and spiders can walk on water

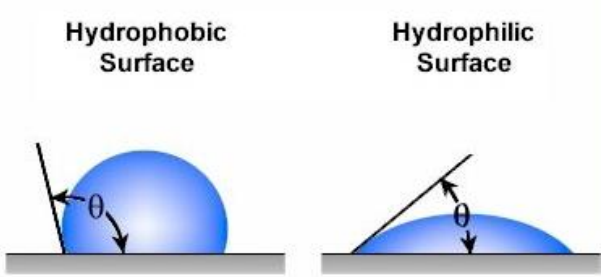
3. Water goes into drops if the tap flow is low enough

4. Contact Angle

The contact angle is the angle made when a liquid-gas surface meets a solid surface.

If a surface is hydrophilic or 'water-loving' (eg. clean glass) then a drop of water will tend to spread out over the surface and the contact angle will be low.

If a surface is hydrophobic 'water-hating' (eg. a greasy baking tray) then a drop of water will bead on the surface and the contact angle will be high.



A neutral surface has a contact angle of 90°.

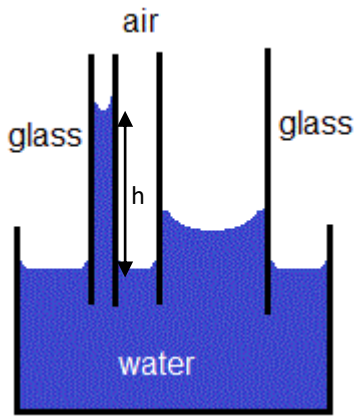
5. Capillary action

If a narrow tube is dipped in water, then the water will rise up inside the tube.

The water molecules are strongly attracted to the surface of the glass tube (adhesive force) and are also strongly attracted to each other (cohesive force).

The water will rise up the tube until the force upwards due to the surface tension is balanced by the force of gravity pulling the column of water downwards.

This effect can be used to measure the surface tension of water, γ



$$\gamma = \tfrac{1}{2} \rho g r h$$

where: ρ is the density of water = 1000 kg/m^3
g is acceleration due to gravity = 9.8 m/s^2
r is the radius of the tube in metres
h is the height of the water (in metres) in the tube above the height of the reservoir

Worked example:

One end of glass tube of radius 2mm is submerged in water. What height will the water climb to in the tube?

The surface tension of water is 0.073 N/m.

Step 1
Rearrange the equation:

		γ		
½	ρ	g	r	h

h = γ / (½ ρ g r)

Step 2
Covert the radius of the tube into metres:

r = 2mm = 2/1000 m = 0.002 m

Step 3
Substitute the levels for the surface tension, density, radius and acceleration due to gravity:

h = 0.073 / (½ x 1000 x 9.8 x 0.002) = 0.0074m

Step 4
Convert the answer to mm:

h = 0.0074m = 0.0074 x 1000 mm = 7.4 mm

Tutorial 2 Homework:

Question 1 – the difference between the heat capacities of land and water

Information: The heat change (ΔQ) is given by:

$$\Delta Q = C_p \, m \, \Delta T$$

where C_p is the specific heat capacity of a substance, m is the mass and ΔT is the change in temperature.

a) **A granite rock has a volume of 1000m^3. If the granite loses 8,000,000 kJ of heat, by how much does its temperature decrease?**

(The density of granite is ρ = 2700 kg/m^3 and the heat capacity of granite is C_p=0.79 kJ/kg^{o}C.)

Step 1 - Calculate the mass of the rock, m.

Step 2 – Rearrange the heat change equation to find the formula for the temperature change ΔT. The diagram below may help you:

	ΔQ	
C_p	m	ΔT

Step 3 – Calculate the temperature change

b) **A lake has a volume of 1000m^3. If the lake also loses 8,000,000 kJ of heat, by how much does its temperature decrease?**

(The density of water is ρ = 1000 kg/m^3 and the heat capacity of water is C_p=4.181 kJ/kg^{o}C.)

c) **Use your results from parts a) and b) to explain why, in winter, it is warmer close to oceans than it is in the middle of continents? (For example the average January temperature in Glasgow is 4°C whereas in Moscow it is -7°C, even though the two cities are at a similar latitude.)**

Question 2 – How tall can a tree grow?

In plants, water is carried through xylem tubes by capillary action. Xylem tubes have a diameter of around 10µm (0.00001m). Assuming capillary action is the only process involved, estimate the maximum height that a tree can grow to.

Stretch: Is your answer roughly what you would expect? If not, can you think of any reasons why not? You may like to read these:

https://www.scientificamerican.com/article/how-do-large-trees-such-a/
https://npand.wordpress.com/2008/08/05/tree-physics-1/

Tutorial 3 – Ice Cream and Other Delicious Colloids

Today's Key Question(s):

- How does the addition of salt affect the bonding between water molecules?
- What is a colloid?

What is the Purpose of Tutorial 3?

- To make ice cream.
- To examine the process of melting ice by adding salt
- To introduce colloids

Today's Homework is:

- Prepare presentation

Making ice cream

Ingredients
¼ cup of milk
¼ cup of cream
1 tbs sugar
½ tsp vanilla essence
4 cups crushed ice
4 tablespoons of salt

Equipment
2 small zip-lock plastic bags
1 large zip-lock plastic bag
1 cup
Towel/cloth or gloves

Method

1. Mix the milk, cream, vanilla and sugar together in the cup.
2. Pour into one of the small bags and seal tightly, allowing as little air to remain in the bag as possible.
3. Place this bag inside the other small bag, again leaving as little air inside as possible and sealing well.
4. Put the two bags inside the large bag and fill the large bag with ice, then sprinkle salt on top. Again let all the air escape and seal the bag.
5. Wrap the bag in the towel or put your gloves on, and shake and massage the bag for 5 to 10 minutes, making sure the ice surrounds the cream mixture.
6. Pour the ice cream into the cup and eat!

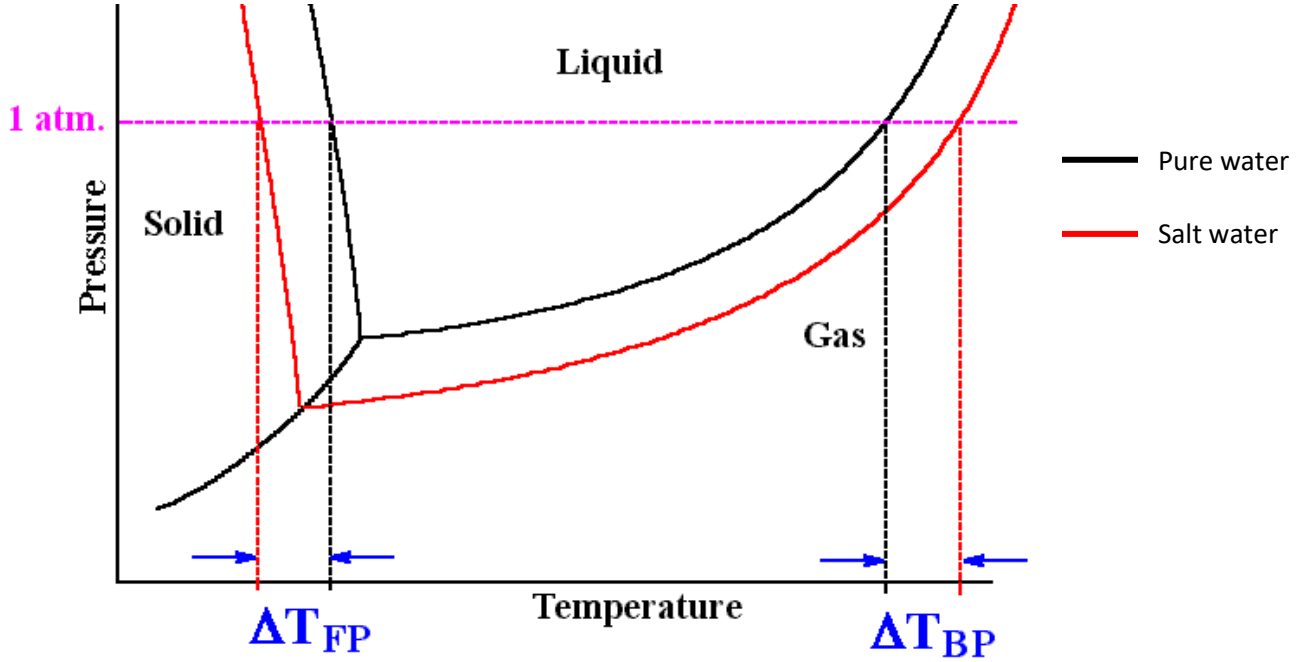
Results

1. What changes did you observe in the cream mixture?

2. What changes did you observe in the ice and salt mixture?

Explanation

The Phase Diagram of Salt Water Compared to Pure Water



Salt water has a lower melting point than pure water because the sodium chloride ions disrupt the bonding between the molecules of water.

Why is salt spread on roads in cold weather?

Introduction to colloids

A colloid is a mixture of substances, where one of the substances consists of tiny dispersed particles suspended in the other substance. (Dispersed means 'separated uniformly throughout'.) The size of the dispersed particles varies from 1nm to 10µm and typically would be small groups of molecules or large molecules like proteins or polymers.

Dispersing medium	Dispersed Phase	Name	Examples
Solid	Solid	Solid Sol	Opal Pearls Gem stones
Solid	Liquid	Gel	Jam
Solid	Gas	Solid Foam	Styrofoam
Liquid	Solid	Sol	Blood Paint
Liquid	Liquid	Emulsion	Hand cream Mayonnaise
Liquid	Gas	Foam	Shaving cream Soap suds
Gas	Solid	Solid Aerosol	Smoke Dust
Gas	Liquid	Aerosol	Spray Deodorant Fog

Look at the pictures of different foods on the first page of this tutorial. Classify them according to their colloid type and add them to the list of examples in the table.

Can you think of any other examples of colloids?

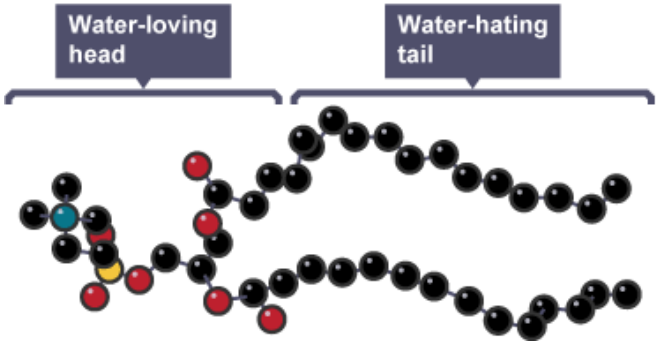
What sort of colloid is ice-cream?

Ice cream is a combination of an emulsion, sol and a foam. The dispersed particles are: milk fat (liquid), ice crystals (solid) and air bubbles (gas). The dispersing medium is the water from the milk.

Emulsifiers

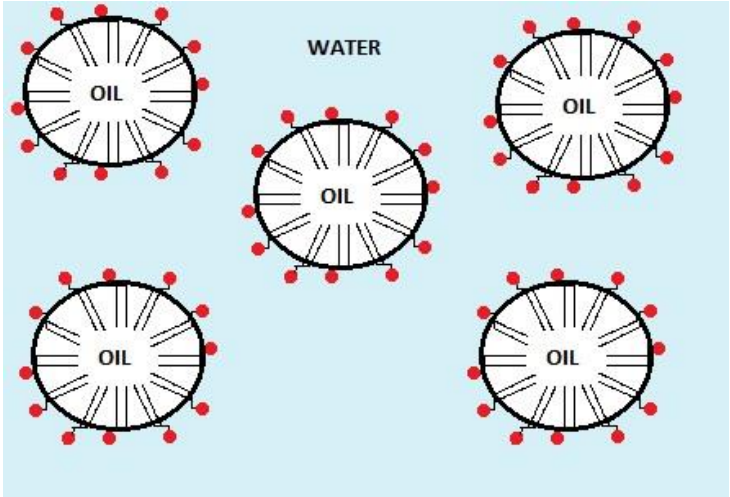
Mayonnaise is an emulsion consisting of tiny droplets of oil dispersed in water (actually vinegar, but it has the same properties as water). Oil and water do not mix well and would tend to separate, so egg yolk is also added to act as an emulsifier.

An emulsifier is a substance which stabilises an emulsion. Emulsifiers consist of molecules with water-loving hydrophilic heads and oil-loving hydrophobic tails.



Emulsifiers are also called surfactants because they reduce the surface tension between the water and the oil.

The water-loving heads interact with the water and the water-hating tails interact with the drop of oil. This stops the oil particles from joining together and eventually separating from the water.



Soap and washing-up liquid are also surfactants. They reduce the surface tension between oil and water, allowing the oil to be washed away.

Tutorial 3 Homework:

Perform a simple, safe experiment or demonstration of one of the properties of water or colloids using equipment found in a typical kitchen.

Prepare a short power-point or poster presentation describing the experiment and explaining the scientific principles demonstrated by the experiment. Include diagrams, photos or a video of your experiment.

For ideas, try these websites:

https://explorable.com/lifting-ice-cube-experiment

http://www.funsci.com/fun3_en/exper2/exper2.htm

http://www.rsc.org/learn-chemistry/resource/res00001719/detergents-soaps-and-surface-tension?cmpid=CMP00005233

http://www.sciencekids.co.nz/experiments/escapingwater.html

http://www.sciencekids.co.nz/experiments/oilandwater.html

http://www.sciencekids.co.nz/experiments/iceoverflow.html

Whenever you perform an experiment, begin by thinking about any possible hazards. Safety is the most important thing, so make sure that you do not attempt anything dangerous and ensure there is an adult present at all times.

Also, remember that if you make a huge mess in your kitchen at home you may risk upsetting a parent. It is usually best to carry out water experiments in a sink or on a draining board. Always get permission from an adult before you begin.

Tutorial 4 – Over to you…

Today's Key Question(s):

- How to communicate science to an audience

What is the Purpose of Tutorial 4?

- Perform your presentation
- Watch other's presentations and ask relevant questions
- Offer feedback on presentations

Today's Homework is:

Draft Final Assignment:

- Choose 3-6 properties of water/colloids/surfaces to include in the final assignment.
- For one of these properties, describe and explain the property including scientific terms and explain the consequences of this property for life on earth.

My Presentation

Title:

What went well:

Ideas for improvement:

Feedback to Others:

Name of presenter:

Title:

What went well:

An idea for improvement:

Name of presenter:

Title:

What went well:

An idea for improvement:

Name of presenter:

Title:

What went well:

An idea for improvement:

Tutorial 5 – Super-hydrophobic Surfaces

Today's Key Question(s):

- What are the properties of hydrophobic surfaces?
- Can we replicate the properties of natural hydrophobic surfaces?

What is the Purpose of Tutorial 5?

- Learn how to approach a scientific paper and read for understanding
- Learn how to search scientific literature (google scholar)
- Learn how to write a scientific review
- Receive feedback on draft assignment

Today's Homework is:

- Final assignment

Reading a scientific paper: Feng, Lin, et al. "Super-hydrophobic surfaces: from natural to artificial." (Advanced materials 14.24 (2002): 1857-1860.)

As a group, you will examine this paper with your tutor.

Your notes

Searching the literature – an introduction to google scholar

https://scholar.google.co.uk/

Google scholar is a free search engine which lets users look for academic articles. Your tutor will demonstrate how to perform a search.

For more tips: https://scholar.google.co.uk/intl/en/scholar/help.html

Writing a scientific review article

A standard structure consists of:

Abstract
This is a summary of all your work. Scientists read the abstract of a paper to decide whether the paper is relevant to them and whether they want to spend time reading it. Therefore, it is an extremely important part of your assignment. Although it comes at the start of an article, it is best to write it last - after you have finalised the rest of your work. Don't be afraid to repeat content (especially from the conclusions) from the rest of your article, but keep it brief. A paragraph or possibly two is plenty.

Introduction
This is a brief overview of the topic and the motivation for the review. Imagine you are trying to persuade someone why your topic is really relevant, exciting and interesting. The final paragraph of your introduction should summarise the structure of the article for the reader (e.g, in Section 2a …….. Section 2b …….. etc)

Body
This contains the main scientific content of the article. It should be split into sections (and subsections if appropriate). It is usually best to write this section first.

As you write, imagine you are trying to explain your topic to someone who is not familiar with it. Think about what information they will need to know to understand it. How can you explain it clearly? Remember their attention may start to wander – how can you keep the reader engaged?

When you include calculations you should carefully explain your method at each step. E.g., 'the density (ρ) was calculated from the mass (m) and the volume (V): $\rho = m / V$).'

When you include pictures or graphs they should be labelled with their figure number and a caption. E.g.

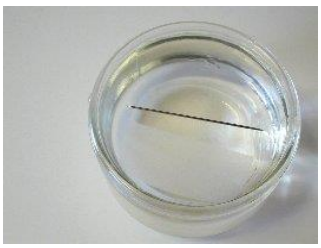


Figure 1
A needle floating in a cup of water

Conclusions
This may be a paragraph or numbered points to sum up your main findings.

References
Advice on how to reference is given in Appendix 1.

Writer's block
Sometimes you may find that you just don't know what to write and can't get started. In this case just write something, it doesn't have to be proper sentences and you may think it is rubbish! It will get you writing and you can always go back and change it later.

More tips: http://www.nuffieldfoundation.org/sites/default/files/writing-a-scientific-review-article-382.pdf

Draft Assignment Feedback:

Tutorial 5 Homework:

Final assignment:

The Weird and Wonderful Properties of Water

- *A review of a selection of different properties of water and their physical consequences.*

Choose 3 to 6 properties of water, colloids or surfaces. For each property of water, colloids or surfaces explain the physical consequences of the property and the relevance to life on earth, including examples of how humans make use of this property where appropriate.

- *Include a phase diagram for either bulk water or water at a surface in at least one of your explanations of the different properties.*
- *The examples should be chosen so that at least one example contains a calculation.*
- *The review may be purely theoretical or may include a write-up of one or more experiments or demonstrations that can be performed using typical kitchen/household equipment.*
  (Suggested word count 600-2000 words)

The Deadline is:

Tutorial 6 – Feedback

What is the Purpose of Tutorial 6?

- Reflect on skills learned on the programme with a view to encouraging resilience
- Receive feedback on final assignment

What are the key questions?

- What strengths have I demonstrated in my work and what areas of development are there left for me to address?
- What steps do I need to take to improve my academic output?

Activity 1 – Marking your own

Using the mark scheme, identify three things you did well and three things you could improve.

What went well?

1.

2.

3.

What could be improved?

1.

2.

3.

Activity 2 – Responding to feedback

Read through your feedback sheet and highlight on your assignment where you received positive feedback (one colour) and areas for improvement (different colour). You might find it helpful to annotate this with a brief comment or two.

Activity 3 – Looking Forwards: Think, Pair Share

1. Think about how you can use this feedback in your future school work.
2. Talk to your partner about how you both plan to make changes to your school work in the future as result of this feedback
3. Share your ideas as a group.

Appendix 1 – Referencing correctly

When you get to university, you will need to include references in the assignments that you write, so we would like you to start getting into the habit of referencing in your Brilliant Club assignment. This is really important, because it will help you to avoid plagiarism. Plagiarism is when you take someone else's work or ideas and pass them off as your own. Whether plagiarism is deliberate or accidental, the consequences can be severe. In order to avoid losing marks in your final assignment, or even failing, you must be careful to reference your sources correctly.

What is a reference?

A reference is just a note in your assignment which says if you have referred to or been influenced by another source such as book, website or article. For example, if you use the internet to research a particular subject, and you want to include a specific piece of information from this website, you will need to reference it.

Why should I reference?

Referencing is important in your work for the following reasons:

- It gives credit to the authors of any sources you have referred to or been influenced by.
- It supports the arguments you make in your assignments.
- It demonstrates the variety of sources you have used.
- It helps to prevent you losing marks, or failing, due to plagiarism.

When should I use a reference?

You should use a reference when you:

- Quote directly from another source.
- Summarise or rephrase another piece of work.
- Include a specific statistic or fact from a source.

How do I reference?

There are a number of different ways of referencing, and these often vary depending on what subject you are studying. The most important to thing is to be consistent. This means that you need to stick to the same system throughout your whole assignment. Here is a basic system of referencing that you can use, which consists of the following two parts:

A marker in your assignment: After you have used a reference in your assignment (you have read something and included it in your work as a quote, or re-written it your own words) you should mark this is in your text with a number, e.g. [1]. The next time you use a reference you should use the next number, e.g. [2].

Bibliography: This is just a list of the references you have used in your assignment. In the bibliography, you list your references by the numbers you have used, and include as much information as you have about the reference. The list below gives what should be included for different sources.

Websites – Author (if possible), title of the web page, website address, [date you accessed it, in square brackets].

E.g. Dan Snow, 'How did so many soldiers survive the trenches?', http://www.bbc.co.uk/guides/z3kgjxs#zg2dtfr [11 July 2014].

Books – Author, date published, title of book (in italics), pages where the information came from.

E.g. S. Dubner and S. Levitt, (2006) *Freakonomics*, 7-9.

Articles – Author, 'title of the article' (with quotation marks), *where the article comes from* (newspaper, journal etc.), date of the article.

E.g. Maev Kennedy, 'The lights to go out across the UK to mark First World War's centenary', *Guardian*, 10 July 2014.

Appendix 2 – University Applications Guidance

For course choices and careers information:	www.brightknowledge.org.uk
For information and statistics on universities and course:	www.unistats.direct.gov.uk
For comprehensive information on universities, including rankings:	www.thecompleteuniversityguide.co.uk

PLEASE NOTE – The Researchers in Schools programme is designed to support the university applications process at your school. The work you complete for the programme should add to your schoolwork rather than detract from it. Please be aware of deadlines and try to manage your workload appropriately. If you are worried about the programme interfering with your schoolwork, then please speak to your teacher.

Subject Specific Top Tips for Strengthening an application

When you are choosing your A levels, think ahead to the subjects you may want to study at university.

For example, if you are applying to study biological sciences, many universities require that you also have an A level in Chemistry and/or Maths or Physics.

For degree courses in Chemistry you usually need Maths A level. For physics it is advantageous if you also take Further Maths.

Engineering usually requires A levels in Physics and Maths.

To be accepted onto a course for Medicine you will need Chemistry and ideally at least three Science/Maths A levels in total.

If you are not yet sure what you want to study at university then make sure you keep your options open by studying 'Facilitating subjects': http://russellgroup.ac.uk/for-students/school-and-college-in-the-uk/subject-choices-at-school-and-college/

Appendix 3 – Scientific Literature

Below are two scientific papers that we will read during the course:

1. Rosenberg, Robert. "Why is ice slippery?" Physics Today 58.12 (2005): 50.
2. Feng, Lin, et al. "Super-hydrophobic surfaces: from natural to artificial. "Advanced materials 14.24 (2002): 1857-1860.

Why Is Ice Slippery?

In 1859 Michael Faraday postulated that a thin film of liquid covers the surface of ice—even at temperatures well below freezing. Neglected for nearly a century, the dynamics of ice surfaces has now grown into an active research topic.

Robert Rosenberg

The freezing of water and melting of ice are among the most dramatic examples of phase transitions in nature. Melting ice accounts for everyday phenomena as diverse as the electrification of thunderclouds, in which the liquid layer on ice chunks facilitates the transfer of mass and charge during collisions between them; frost heave powerful enough to lift boulders from the ground (see PHYSICS TODAY, April 2003, page 23); and, of course, slippery surfaces.

Everyday experience suggests why ice surfaces should be slippery: Water spilled on a kitchen floor or rainwater on asphalt or concrete can create the same kinds of hazards for walkers and drivers that ice can. Presumably, the liquid makes the surface slippery because liquids are mobile, whereas solid surfaces are relatively rigid. Asking why ice is slippery is thus roughly equivalent to asking how a liquid or liquid-like layer can occur on the ice surface in the first place.

Pressure melting

The common perception, even among those with a moderate knowledge of science, is that skaters slide more easily on ice than on other solids because ice melts under their skates' pressure to produce a film of water. Water is denser than ice and occupies about 10% less volume per mole. So according to Le Chatelier's principle, an increase in pressure results in melting the ice and decreases the sample's volume. That is, if melting had occurred by itself, it would have resulted in a decrease in pressure.

The science of the observation originated in 1850, when James Thomson developed an expression for the linear dependence of the freezing point depression on pressure. His brother William, later Lord Kelvin, verified that result experimentally. Neither, however, referred to ice skating. That inference had to wait until 1886, when a young engineer named John Joly worked on the problem and referred to Thomson's results. Joly pointed out that the pressure of a skater's blade edge is so great because it touches the ice over so small an area. He calculated a pressure of 466 atmospheres and a corresponding melting point of −3.5 °C, a temperature that creates a film of water on which the skater slides (see figure 1).

Osborne Reynolds also invoked pressure melting in 1899 to explain ice skating. But his inspiration came from watching solder melt when it was pressed against a soldering iron. Reynolds assumed that a similar pressure produced a liquid film on ice that made skating possible.[1]

Joly never explained how skating might be possible at temperatures lower than −3.5 °C. And there's the problem. The optimum temperature for figure skating is −5.5 °C and for hockey, −9 °C; figure skaters prefer slower, softer ice for their landings, whereas hockey players exploit the harder, faster ice. Indeed, skating is possible in climates as cold as −30 °C and skiing waxes are commercially available for such low temperatures. In his 1910 account of his last expedition to the South Pole, Robert Falcon Scott tells of skiing easily at −30 °C. But Scott's chief scientist, Edward Wilson, described the snow surface as sandlike at −46 °C. Based on his soldering-iron experiments, Reynolds might have anticipated that frictional melting must play a role as well as pressure melting, inasmuch as heat caused the melting of his solder. But surprisingly, even with little evidence in its favor, pressure melting remained the dominant explanation of the slipperiness of ice for nearly a century.

Frictional heating

Frank P. Bowden and T. P. Hughes suggested the frictional heating alternative to pressure melting in a 1939 article.[2] Remarkably, no one before them had calculated that a skier's pressure on snow is insufficient to cause melting at low temperatures. Bowden and Hughes carried out an extensive set of experiments in a cave dug out of the ice above the research station in Jungfraujoch, Switzerland, at an altitude of 3346 meters. Cave temperatures never rose above −3 °C, and the team achieved lower temperatures by using solid carbon dioxide and liquid air. Using surfaces of wood and metal, they measured both static and kinetic friction. Because metal skis showed higher friction than wooden skis, the researchers concluded that frictional heating was responsible for melting the ice; frictional heating would be affected by the conductivity of the skis, but pressure melting would not. Pressure melting seemed to play a role only near the melting point.

Geophysicist Samuel Colbeck made a series of contributions to the debate in a series of papers published between 1988 and 1997.[3] In the earliest, he argued against the pressure-melting explanation on the basis of calculations of the pressure required to melt ice at low temperatures and on the basis of the phase diagram, which shows the transition of ice from one solid phase to another at −22 °C (see figure 2). The argument confirmed again how

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Figure 1. An ice skater exerts pressures on the order of a few hundred atmospheres on the ice surface, enough to reduce the melting temperature by only a few degrees. Premelting—the development of a liquid-like surface layer at temperatures below freezing—and frictional heating of the ice as skaters move around must account for ice's slipperiness at the wide variety of subzero temperatures found in nature. (*Ice Skating*, by Hy Sandham, 1885, courtesy of the Library of Congress.)

pressure melting leaves unexplained the ability to ski and skate at temperatures as low as −35 °C. Colbeck also pointed out that the pressure required to cause melting at the lower temperatures would squeeze the liquid film to such an extent that the friction generated, far from facilitating skating, would resist it.

He and coworkers then provided experimental evidence for frictional heating by fastening a thermocouple to a skate blade (and later to the bottoms of skis). The increase in temperature with velocity, they observed, was consistent with frictional, localized heating of the ice underfoot to create a thin water layer. Were pressure melting—an endothermic process—the dominant contribution, the researchers would have expected a decrease in temperature.

Melting below zero

Neither pressure melting nor frictional heating explains why ice can be so slippery even while one is standing still on it. What evidence is there for the existence of liquid at the surface—even at temperatures below zero? Although he was apparently unconcerned with ice skating and frictional effects on surfaces, Michael Faraday took the first steps toward answering that question. In a discourse given at the Royal Institution on 7 June 1850, he devoted most of his remarks to elegant experiments he had conducted on regelation, the freezing together of two ice cubes when they come into contact. Faraday suggested that a film of water on ice will freeze when placed between the two pieces of ice, although the film remains liquid on the surface of a single piece. The liquid layer that coats the ice cubes, he argued, must play a critical role in freezing them together. Observations of wet snow freezing may have inspired Faraday's claims, but his experiments were nevertheless the first to investigate the phenomenon of premelting, the development of a liquid layer that forms on solids at temperatures below the bulk melting point.

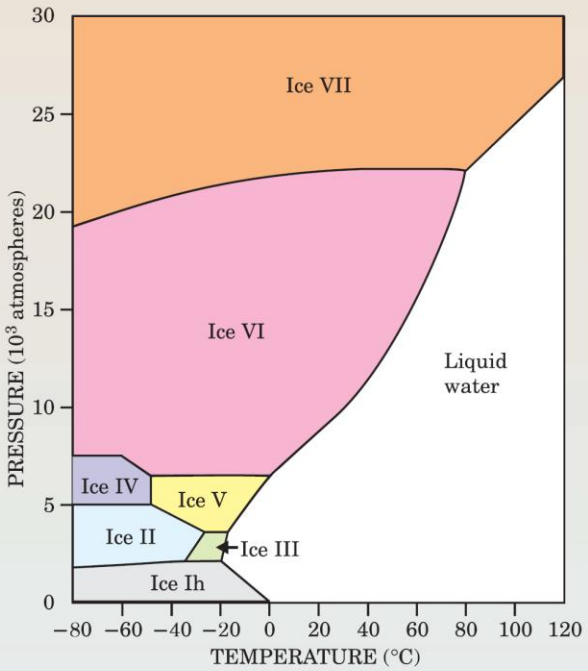

Figure 2. Phase diagram of H_2O. Ice exhibits a rich variety of crystalline and glassy structures in at least 11 distinct phases (7 are shown here) at different pressures and temperatures. The ice–water phase transition is simpler. The melting temperature increases steadily with pressure except at low pressures, where the familiar hexagonal ice-Ih structure is less dense as a solid than a liquid. (Diagram courtesy of Steven I. Dutch, University of Wisconsin at Green Bay.)

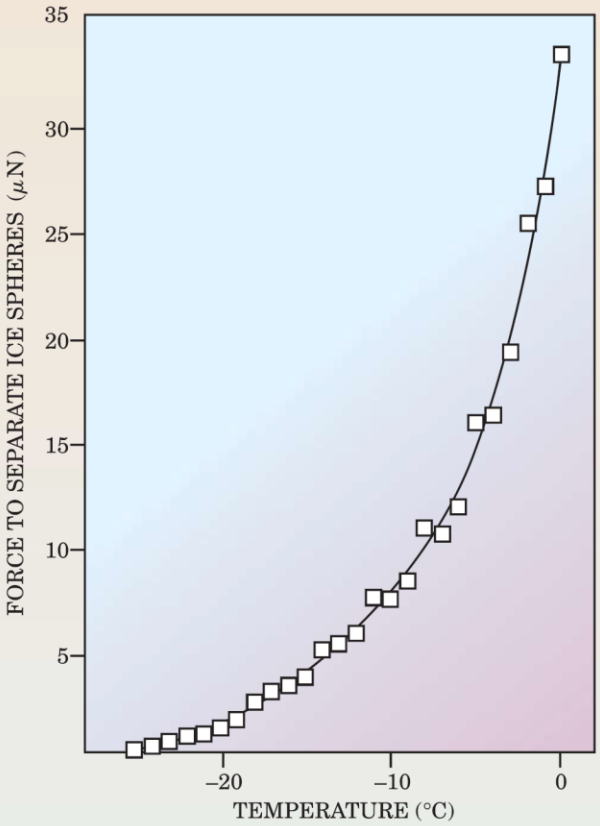

Figure 3. In a series of 1957 experiments, Charles Hosler and colleagues measured the force required to pull apart a pair of ice spheres in equilibrium and touching each other. The force increased as the temperature increased, an indication that warmer—though still subzero—temperatures form increasingly thick liquid-like layers on each sphere's surface. (Data adapted from ref. 7, C. L. Hosler et al.)

Not everyone at the time was convinced. Shortly after Faraday's published account appeared in 1859,[4] James Thomson took the position that the regelation Faraday observed was due to pressure on the ice cubes. The resulting absorption of the heat of melting caused the refreezing, he argued, although he provided no additional experimental evidence. Later that year, Faraday replied to Thomson's views, arguing for the presence of a liquid layer near the melting point mainly on the basis that ice cannot be superheated, whereas liquid water can be superheated and supercooled.[5]

An 1860 article offered a more complete rebuttal, with new experimental results. Faraday prepared two pieces of ice, each attached by a thread to lead weights that submerged them in a water bath maintained at 0 °C. When displaced laterally, they returned to their original places "with considerable force." "If brought into the slightest contact, regelation ensued, the blocks adhered, and they remained adherent notwithstanding the force tending to pull them apart."[5] Thomson, unconvinced, replied yet again. J. Willard Gibbs, in a long, though little noticed, footnote to his famous 1876 paper on thermodynamics, took account of the work and found that his conclusions were "in harmony with the opinion of Professor Faraday."

Remarkably, despite the elegant and simple experiments and published support from Gibbs, Faraday seems to have been forgotten, and Thomson's views prevailed. Thomson's purely verbal arguments held sway for nearly a century. Indeed, it wasn't until 1949 that a modern scientist, C. Gurney, suggested that an intrinsic liquid film plays a role in the slipperiness of ice. Gurney hypothesized that molecules, inherently unstable at the surface due to the lack of other molecules above them, migrate into the bulk of the solid until the surface becomes unstable, which prompts the formation of a liquid phase. Two years later, W. A. Weyl accepted Faraday's concept of a liquid film on the surface of ice and developed a model based on the differences between the molecular arrangement of water molecules in the bulk and on the surface.[6]

In the mid-1950s, different research teams put the concept on a quantitative footing by performing experiments reminiscent of Faraday's own investigations on the freezing together of ice cubes. In each case they measured the force of adhesion between two spheres of ice allowed to touch.[7] Charles Hosler's group at the Pennsylvania State University achieved particularly compelling results (see figure 3). The group compiled data from a series of experiments, each conducted at a different temperature between −25 °C and 0 °C at the vapor pressure of ice, to construct a smooth curve of the forces required to pull ice spheres apart. At vapor pressures below ice saturation, no adhesion occurred below −4 °C. The researchers inferred that the expected roughness of the surfaces was removed by the presence of a liquid film whose thickness was sufficient to provide a smooth surface of contact.

In the years since Weyl's and Gurney's papers appeared, experimentalists and theoreticians have done much to understand the relative contributions of pressure melting, frictional heating, and the presence of liquid-like films on surfaces of ice. Each mechanism plays a role that depends on the temperature (for a review, see reference 8). Of those contributions, the precise nature of the liquid-like layer has been the most elusive.

Measuring thickness

In 1963 J. W. Telford and J. S. Turner carried out a series of regelation experiments, each at a different temperature, in which a wire under pressure slowly migrates through ice.[9] The experiment was a quantitative version of an earlier one used to support the hypothesis of pressure melting. Using a contact on the wire as part of a potentiometer circuit, the researchers precisely measured the velocity and found that it increased linearly with temperature from −3.5 °C to −0.5 °C. From −0.5 °C to the melting point, the velocity of the wire's passage increased sharply. For the force applied and the size of wire used, they calculated a melting-point decrease of −0.5 °C due to pressure melting, yet another indication that pressure melting was not responsible for the passage of the wire through ice below that temperature. The quasi-static nature of the motion meant frictional processes played no role either. Nor was creep—the slow mechanical deformation of a solid—responsible for the wire's motion, to judge from the activation energy they calculated.

Rather, Telford and Turner interpreted their results in terms of the flow of a thin Newtonian shear layer of a viscous fluid around the wire, and calculated a layer thickness that satisfied a function $(T - T_m)^{-1/2.4}$, where T is the temperature in kelvin, and T_m is the melting point temperature. In 1980, R. R. Gilpin[9] extended Telford and Turner's work to the broader temperature range of −35 °C to −0.005 °C. At −35 °C, the calculated viscosity of the water in the liquid layer is at most a few times greater than that of bulk water. Gilpin found both a slow mode and a fast mode for the wire's motion, in accord with Telford

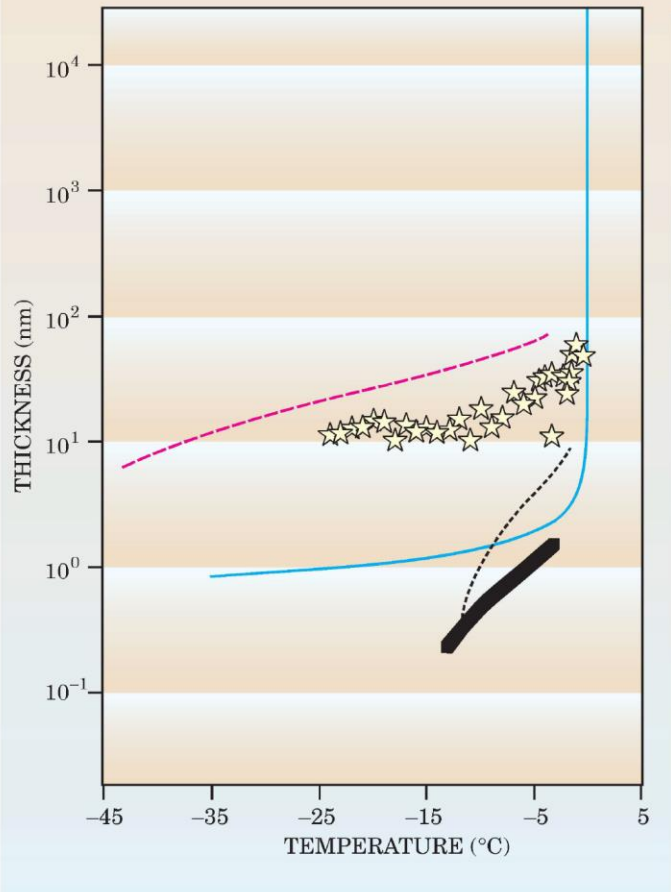

Figure 4. A compilation of data from different experimental approaches illustrates the variation of thicknesses of the liquid-like layer on ice obtained by different methods. Proton backscattering data (red dashed line) are adapted from ref. 13; x-ray scattering data using a glass interface (black dashed line) and a silicon interface (black bold line), from ref. 14, H. Dosch et al. and S. Engemann et al.; atomic-force microscopy measurements (stars) courtesy of Hans-Jurgen Butt; and regelation data (blue solid line) from ref. 9, R. R. Gilpin.

and Turner, and fit the velocity as a function of temperature in the slow mode to the same function. The phenomenon occurred at temperatures well below −22 °C.

In 1969, Michael Orem and Arthur Adamson found yet more surprising evidence for the presence of a liquid-like layer on the surface of ice when they compared the physical adsorption of simple hydrocarbon vapors on ice with their adsorption on a liquid-water surface. Above −35 °C the adsorption isotherm of *n*-hexane on the surface of ice tracks that of the same vapor on the surface of liquid water, but not at temperatures below −35 °C. The entropy and enthalpy of adsorption also track the pattern of liquid water above −35 °C, but not below. Orem and Adamson interpreted their results as indicating that the onset of ice's surface premelting is at −35 °C.

That liquid layers persist to such low temperatures can have striking environmental consequences. In the 1990s, chemistry Nobel laureate Mario Molina and coworkers, for instance, attributed the adsorption of hydrochloric acid on polar stratospheric clouds to the existence of a liquid-like layer on ice. The adsorption plays a role in the destruction of ozone.[10]

Since the mid-1960s, a variety of experimental approaches, performed under a variety of conditions, have been brought to bear on the premelting problem to determine the temperature range and thickness of any postulated layer. (For review of the literature on the topic up to that time, see reference 11.) Unfortunately, those different experimental conditions, ranging from high vacuum to the equilibrium vapor pressure of ice, make comparison between experimental results difficult (see figure 4).

Nuclear magnetic resonance (NMR) provided evidence for a liquid layer on the surface of ice: Below the melting point there is a narrow absorption line, not the broad line one would expect from a periodic solid.[12] Molecules at the surface between −20 °C and 0 °C rotate at a frequency five orders of magnitude greater then those in bulk ice and about 1/25 as fast as those in liquid water. The self-diffusion coefficient is two orders of magnitude larger than that in bulk ice.

Using proton backscattering, researchers in 1978 found surface vibrations of the oxygen atoms roughly 3.3 times the amplitude of their value in the bulk, and an amorphous layer 10 times thicker than what NMR measurements had estimated.[13] But, unlike NMR, the proton backscattering measurements were made under high vacuum, a condition markedly different from the finite vapor pressures at which surface melting typically occurs.

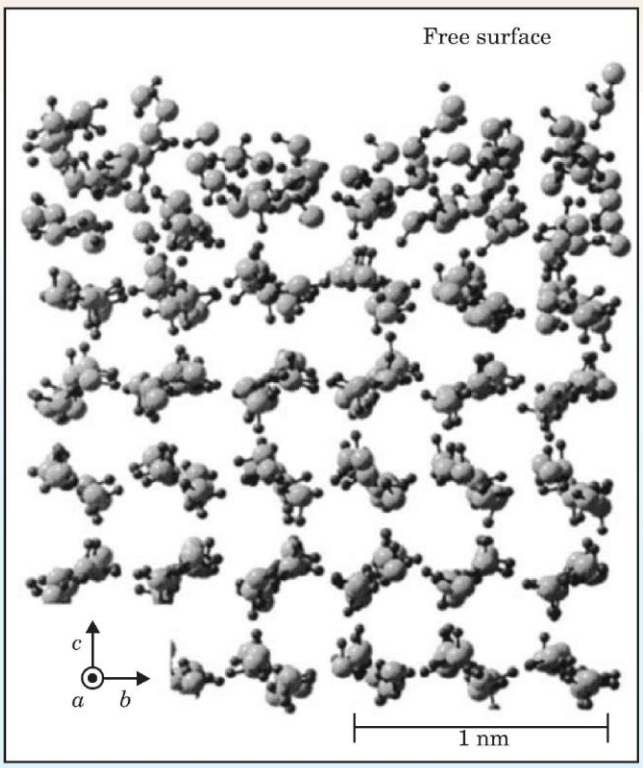

Figure 5. Molecular-dynamics simulations calculate the variation from the periodic lattice that surface molecules suffer in the premelted phase at -20 °C. The large gray circles represent oxygen atoms and the small black circles, hydrogen atoms; the thin lines represent covalent bonds that connect them. (Adapted from ref. 17.)

X-ray diffraction offers perhaps the most convincing evidence for the liquid-like layer on the surface of ice.[14] Work done in 1987 found that the intermolecular distance on the ice surface is slightly smaller than it is in liquid water, whose intermolecular distances are, of course, smaller than ice's are. In the mid-1990s Helmut Dosch (Max Planck Institute for Metal Research and the University of Stuttgart) and coworkers published a series of more detailed papers on their study of ice surfaces using glancing-angle x-ray scattering. This group found a liquid-like layer on the different crystallographic ice surfaces between −13.5 °C and 0 °C. Their model describes a surface layer that exhibits rotational disorder with intact long-range positional order well below the surface melting temperature. At the surface-melting temperature, a completely disordered layer exists on the surface above the rotationally disordered layer.

In 2004 Harald Reichert, Dosch, and colleagues studied the interface between ice and solid silicon dioxide using x-ray reflectivity and calculated the thickness and density of that liquid-like layer between −25 °C and 0 °C. The density of the surface phase turned out to vary from the typical value of liquid water at the melting point to 1.17 g/cm^3 at −17 °C—close to that of the high-density form of amorphous ice, and reminiscent of Yoshinori Furukawa's results on the intermolecular distance measured between oxygen atoms in the surface layer.

In 1998, using atomic force microscopy, Astrid Döppenschmidt and Hans-Jurgen Butt, both at the Gutenberg University in Mainz, Germany, measured the thickness of the liquid-like layer on ice.[15] Capillary forces on the liquid surface prompted the AFM's cantilever tip to jump into contact with the solid ice once it reached the much softer layer's level. The upper limit in thickness of the liquid-like layer varied from 12 nm at −24 °C to 70 nm at −0.7 °C. Their results indicated that at about −33 °C surface melting starts.

Döppenschmidt and Butt also found that the surface layer is thicker when salt is present. Indeed, Yale University's John Wettlaufer argues that the presence of impurities in the surface films can explain the wide thickness variation in the liquid-like film on ice and the temperature dependence of the thickness that researchers have found using various techniques.[16] Wettlaufer describes the transition with increasing temperature from a disordered solid to a partly structured quasi-liquid to a fluid; hence the difficulty of finding consistent descriptions with different techniques. Further progress toward understanding the surface of ice may be dependent on performing several kinds of measurements on the same surface under comparable conditions.

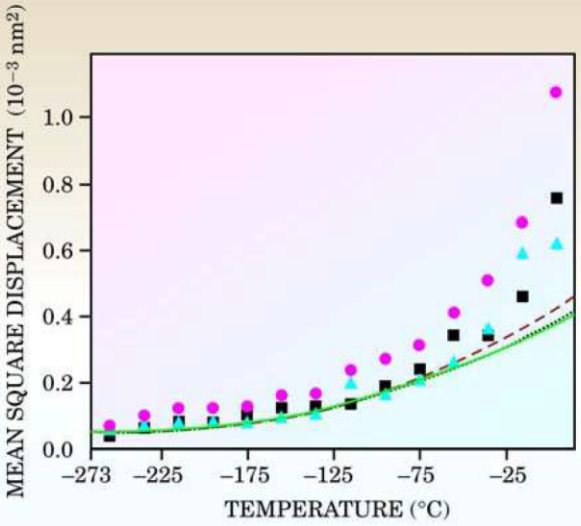

Figure 6. With fewer chemical bonds to hold them in place, surface molecules vibrate with greater amplitude than those located in the bulk crystal. The mean square displacement (MSD) of oxygen and hydrogen atoms on the outermost surface of ice reflects that thermal vibration and increases as a function of temperature. The squares, triangles, and circles represent the average MSD of the outermost oxygen bilayer of the crystal surface along the *a*-, *b*-, and *c*- axes, respectively; the dotted, dashed, and solid lines indicate the MSD of bulk ice along those axes. (Adapted from ref. 17.)

The nature of the liquid-like layer is not clear from experimental measurements, so theorists have tried to clarify the situation. In 2004 Tomoko Ikeda-Fukazawa (Japan Science and Technology Agency) and Katsuyuki Kawamura (Tokyo Institute of Technology) performed molecular dynamics simulations of the ice-Ih surface as a function of temperature.[17] Figure 5 illustrates the melted or liquid-like surface layer calculated in a simulation of the surface at −20 °C.

The periodic structure breaks down and the molecular layers adopt a more amorphous reconstruction in response to the reduced number of chemical bonds holding the surface molecules in place. Atoms in the outermost surface vibrate with greater amplitude as a function of temperature than atoms in the interior lattice (see figure 6). Surface melting is attributable to the interaction of the vibrational motion of the surface molecules with the interior bulk molecules.

Beyond ice

The phenomenon of surface melting is not limited to ice. In 1985 Joost W. M. Frenken and J. F. van der Veen of the Institute for Atomic and Molecular Physics in Amsterdam fired a beam of ions against a lead crystal and monitored the scattering.[18] Based on how the ions backscattered into their energy detectors, the researchers deduced that lead has a melting transition far short of its bulk melting temperature (327 °C) and found a phase in which the surface became completely disordered at 307 °C. The surface film's thickness rises logarithmically with temperature. Since then, experiments have verified liquid-like surface layers on metals, semiconductors, molecular solids, and rare gases.

The slipperiness of other solids is another matter. Although diamond does not exhibit surface melting at room temperature, it does have, below its melting point, a kinetic coefficient of friction even smaller than ice—the friction coefficient, measured in air, can be as low as 0.1 for diamond-like carbon films sliding on each other. Friction coefficients are highest (about 0.6) on diamond measured in vacuum, with successively lower values measured in hydrogen, oxygen, and water-vapor atmospheres—the presence of gases serves to tie up reactive dangling bonds on a surface. The friction coefficient of ice sliding on ice, in comparison, varies between 0.1 and 1.5, depending on sliding velocity.

In an argon atmosphere, lead, zinc, tin, and cadmium powders all exhibit lower friction from 10 to 100 °C below their melting points when used as lubricants for steel rubbing against steel. Indeed, researchers have modeled the

lubrication between two metal surfaces in which one has a low melting temperature and found evidence that frictional melting provides lubrication by a liquid film. Whether these observations or the model support the notion that a frictionally melted layer would permit skating on a metal surface near or below its melting point is surely an open question.

I am grateful to Brian Hoffman and Richard Van Duyne for the initial impetus to write this article, to Samuel Colbeck for many valuable discussions, and to Franz Geiger and Louis Allred for a careful reading of an early draft.

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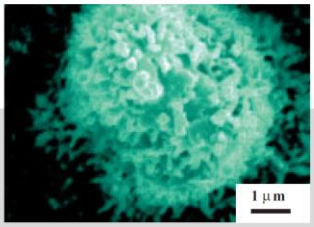
ADVANCED MATERIALS

Super-Hydrophobic Surfaces: From Natural to Artificial**

By *Lin Feng*, *Shuhong Li*, *Yingshun Li*, *Huanjun Li*, *Lingjuan Zhang*, *Jin Zhai*, *Yanlin Song*, *Biqian Liu*, *Lei Jiang*,* and *Daoben Zhu*



Super-hydrophobic surfaces, with a water contact angle (CA) greater than 150°, have attracted much interest for both fundamental research and practical applications. Recent studies on lotus and rice leaves reveal that a super-hydrophobic surface with both a large CA and small sliding angle (α) needs the cooperation of micro- and nanostructures, and the arrangement of the microstructures on this surface can influence the way a water droplet tends to move. These results from the natural world provide a guide for constructing artificial super-hydrophobic surfaces and designing surfaces with controllable wettability. Accordingly, super-hydrophobic surfaces of polymer nanofibers and differently patterned aligned carbon nanotube (ACNT) films have been fabricated.

1. Introduction

The wettability of solid surfaces is a very important property, and is governed by both the chemical composition and the geometrical microstructure of the surface.[1] The generation by UV illumination of a super-hydrophilic TiO_2 surface with a contact angle (CA) for water of 0° has attracted significant attention.[2] This material has already been successfully applied as a transparent super-hydrophilic coating with anti-fogging and self-cleaning properties.[3] Currently, super-hydrophobic surfaces with water CA higher than 150° are arousing much interest because they will bring great convenience in daily life as well as in many industrial processes.[4] Various phenomena, such as snow sticking, contamination or oxidation, and current conduction, are expected to be inhibited on such a surface.[5]

Conventionally, super-hydrophobic surfaces have been produced mainly in two ways. One is to create a rough structure on a hydrophobic surface (CA > 90°), and the other is to modify a rough surface by materials with low surface free energy. Up to now, many methods have been developed to produce rough surfaces, including solidification of melted alkylketene dimer (AKD, a kind of wax),[6] plasma polymerization/etching of polypropylene (PP) in the presence of polytetrafluoroethylene (PTFE),[7] microwave plasma-enhanced chemical vapor deposition (MWPE-CVD) of trimethylmethoxysilane (TMMOS),[8] anodic oxidization of aluminum,[9] immersion of porous alumina gel films in boiling water,[10] mixing of a sublimation material with silica or boehmite,[5] phase separation,[11] and molding.[12] To obtain super-hydrophobic surfaces, coating with low-surface-energy materials such as fluoroalkylsilane (FAS) is often necessary.[5,9–12] While the water CA has commonly been used as a criterion for the evaluation of hydrophobicity of a solid surface, this alone is insufficient to assess the sliding properties of water droplets on the surface.[13] A fully super-hydrophobic surface should exhibit both high CA and low sliding angle (α), where α can also be expressed as the difference between advancing and receding contact angle (hysteresis).

2. The Effect of a Multiscale Plant Surface on Anti-Adhesion of Water

The self-cleaning effect of some plant leaves is of great interest for practical applications. The observation of hydropho-

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bicity related to the topology of the surface of a plant leaf was previously reported by Barthlott and Neinhuis.[14] It was believed that this unique property is based on surface roughness caused by the micrometer-scale papillae and the epicuticular wax.[15] However, the fundamental mechanism remains unclear. Recently, we reported a novel finding of micro- and nanoscale hierarchical structures on the surface of a lotus leaf, i.e., branch-like nanostructures on top of the micropapillae.[16] These structures can induce super-hydrophobic surfaces with large CA and small α. Figure 1a shows a typical large-scale

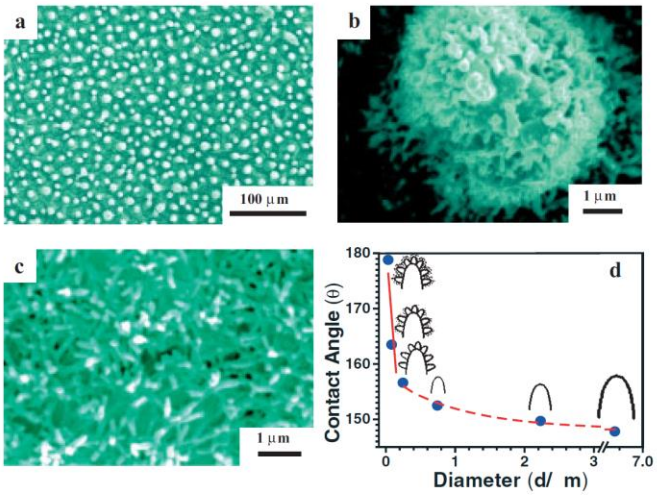

Fig. 1. a) Large-area SEM image of the surface of a lotus leaf (*Nelumbo nucifera*). Every epidermal cell forms a papilla and has a dense layer of epicuticular waxes superimposed on it. b) Enlarged view of a single papilla from (a). Reproduced from [16] with permission from the Chinese Physical Society. c) SEM image of the lower surface of the lotus leaf. d) The fitted curve based on calculated data (contact angle, in degrees, against the mean outer diameter of protruding structures, in micrometers).

scanning electron microscopy (SEM) image of the surface of a lotus leaf. Many papillae were found on this surface in a random distribution with diameters ranging from 5 to 9 μm. CA and α on the surface of this lotus leaf were about $161.0° \pm 2.7°$ and 2°, respectively. Figure 1b shows a high-resolution SEM (HRSEM) image of a single papilla, where hierarchical structures in the form of branch-like nanostructures with average diameters of 124.3 ± 3.2 nm on every papilla are clearly observed. Nanostructures were also found on the lower surface of the lotus leaf (Fig. 1c), which would effectively prevent the attachment of water droplets here also, should the underside of the leaf get wet. These nanostructures on the surface of the lotus leaf, especially on the top of the micropapillae, may be very useful for super-hydrophobicity.

A model of such a surface with super-hydrophobicity and multiscale character can be inferred as described by Adamson and Gast.[17] The surface roughness was considered on the top of the papillae. Since the hierarchical structures on the surface of the lotus leaf are very similar to the description of the triadic Koch curve in fractal geometry,[18] the fractal formula was used to calculate the roughness factor. By changing the roughness factor, a mathematic model was evolved as follows to describe the relationship between CA on a rough surface (θ_f) and that on a smooth surface of the same solid (θ):

$$\cos\theta_f = f_s(L/l)^{D-2}\cos\theta - f_v \quad (1)$$

Here, $(L/l)^{D-2}$ is the surface roughness factor, where L and l are, respectively, the upper and lower limit scales of the fractal behavior of the surface, and D is the fractal dimension. In the case of the lotus leaf, L and l correspond to the size of the diameters of the papillae and branch-like nanostructures, respectively. In the triadic Koch curve model, the value of D in three-dimensional space was found to be about 2.2618, and the value of L/l equal to 3^n. The value of n is determined by the object acting on the fractal structures. The surface roughness factor became larger with increasing n value. Accordingly, if the upper limit scale L is certain, the larger the value of n, the smaller that of l. In Equation 1, f_s and f_v are the fractions of the surface under the water droplet occupied by solid material and air, respectively ($f_s + f_v = 1$). Here f_s and f_v were evaluated from the SEM image (Fig. 1a) as 0.2056 and 0.7944, respectively, and the value of θ was $104.6° \pm 0.5°$ measured from the primary component of epicuticular waxes.[19] Therefore, the value of θ_f can be calculated from Equation 1 as 147.8°, 149.7°, 152.4°, 156.5°, and 163.4° for $n = 0$, 1, 2, 3, and 4, respectively. Using these results, the contact angle (θ) was plotted as a function of diameter as in Figure 1d. The point corresponding to the situation on the surface of a lotus leaf can be found on the curve. CA was about 160°, from which the diameter was about 128 nm, in the scale of nanostructure. This model can be applied to all types of hydrophobic surfaces.

3. High Contact Angle Induced by Nanostructures

Nanostructures on a solid surface are very important for super-hydrophobicity, which can induce a high CA. Recently, we reported the preparation of densely packed aligned carbon nanotube (ACNT) films with pure nanostructures.[20] Figures 2a and 2b show SEM images of the top and cross-sectional views of the as-grown densely packed ACNTs, respectively. These nanotubes are aligned almost normal to the substrate surface with a fairly uniform external diameter of about 60 nm. The CA on these nanostructured ACNT films was $158.5° \pm 1.5°$. Furthermore, the as-grown ACNT films exhibited super-"amphiphobicity" after fluoroalkylsilane coating, that is, CAs for both water and oil were larger than 160°. This phenomenon was believed to be due to the nanostructures and the presence of fluoroalkylsilane groups. Based on this study, we are currently developing a novel template-based extrusion method to synthesize a super-hydrophobic surface of polyacrylonitrile (PAN) nanofibers.[21] Figure 2c shows a cross-sectional SEM image of as-synthesized PAN nanofibers. Aligned PAN nanofibers with end tips were obtained, the average diameter of the nanofiber tips and interfiber distance being about 104.6 nm and 513.8 nm, respectively.

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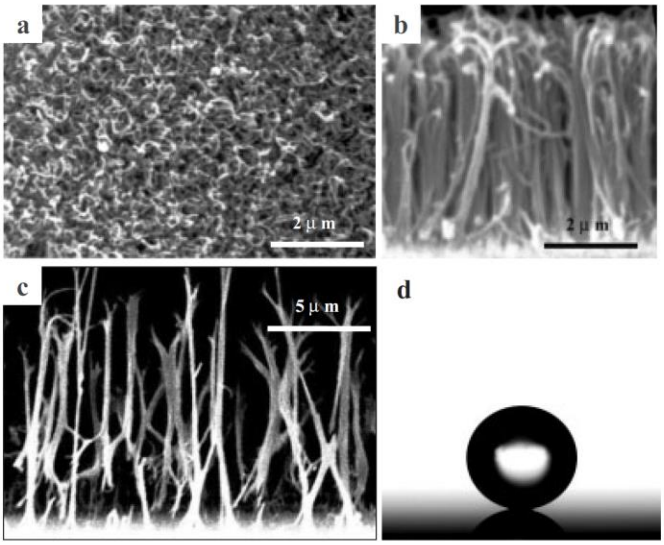

Fig. 2. a,b) SEM images of densely packed ACNT films (top view (a) and cross-sectional view (b)). Reproduced from [20] with permission from Wiley-VCH. c) SEM image of the cross section of PAN nanofibers. d) Shape of water droplet on the surface of as-synthesized PAN nanofibers. Reproduced from [21] with permission from Wiley-VCH.

These PAN nanofibers had a nanostructure similar to that of the ACNTs but a much lower density. This structure contributed to the very large fraction of air in the surface, which is essential to super-hydrophobicity.[22] As a result, the value of CA on the surface of PAN nanofibers was as high as $173.8° \pm 1.3°$, even without any modification of this surface by materials of low surface energy (Fig. 2d). The needle-like structure proved to be an ideal surface for super-hydrophobicity.

The study of ACNT films and PAN nanofibers revealed that nanostructures on the surface are effective for obtaining large CAs. These results can be explained by Equation 1, i.e., without the terms f_s and f_v, the surface roughness can be enhanced by the nanostructures themselves, thus yielding a large CA. However, the value of α, the difference between advancing and receding CAs, was higher than 30° for water on both untreated ACNT films and a surface of PAN nanofibers. The reason is that water droplets are normally pinned on these nanostructured surfaces. More importantly, we are about to report for the first time the creation of a super-hydrophobic nanostructured surface from an amphiphilic polymer.[23] This phenomenon is attributed to the rearrangement of poly(vinyl alcohol) (PVA) molecules during the extruding process, as well as the reorientation of hydrophobic groups ($-CH_2-$) at the air–solid interface. The study might open up new perspectives in the preparation of super-hydrophobic surfaces from various types of materials.

4. Low Sliding Angle Caused by Nano- and Microstructures

The hierarchical structures created by nanostructures on microstructures give a novel approach to constructing super-hydrophobic surfaces as in the natural world. Accordingly, lotus-like ACNT films with both large CA and small α have been prepared. Figure 3a shows the SEM image of the top view of the lotus-like ACNT films; the average diameter of

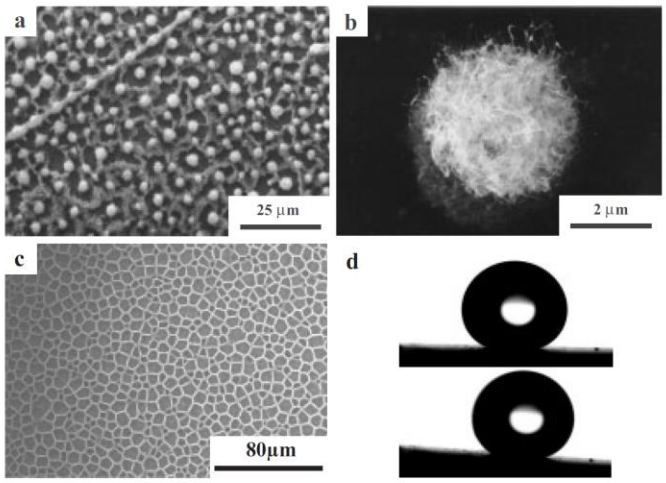

Fig. 3. a) SEM image of the top view of the lotus-like ACNT films. b) Enlarged view of a single papilla from (a). c) SEM image of the large-area honeycomb-like ACNT films. Reproduced from [24a] with permission from the American Chemical Society. d) Sliding behavior of a water droplet on the as-prepared lotus-like ACNT films (drop weight, 9 mg; tilt angle of surface, 3°; high-speed photograph with 20 ms per frame).

the papillae and their separation were about 2.89 ± 0.32 μm and 9.61 ± 2.92 μm, respectively. The HRSEM image of one single micropapilla with nanostructures is shown in Figure 3b. The outer diameter of the carbon nanotube was in the range from 30 to 60 nm (estimated from transmission electron microscopy (TEM) images of single carbon nanotubes, not shown here). CA on these ACNT films was about 166°, and α was about 3°. The lotus-like ACNT films have both a larger CA and a lower α, namely, anti-adhesion to water. These two aspects are both important for a super-hydrophobic surface. In comparison, the value of α on the lotus-like ACNT films was much lower than that on densely packed ACNT films with only nanostructures. The reason is that discrete contact was built up between the solid and liquid surfaces, which impacts the contour, length, and continuity of the triple contact line (TCL) around water droplets, consequently leading to the drastic decrease of α.[6,7]

Based on this study, other patterned surfaces, including honeycomb-like, island-like, and post-like ACNT films with micro- and nanostructures, were prepared.[24] Figure 3c shows a typical SEM image of as-synthesized large-area honeycomb-like ACNTs, whose surface exhibited super-hydrophobicity with high CA $163.4° \pm 1.4°$ and low α (less than 5°). The diameter of the honeycombs ranged from 3 to 15 μm. TEM investigation suggested that these honeycombs consisted of multi-walled nanotubes with a hollow inside; the diameter of a single carbon tube was about 25–50 nm. Figure 3d shows the sliding behavior of a water droplet on the as-prepared lotus-like ACNT films. Water droplets were unstable with respect to remaining on the surface, and spontaneously rolled off with a slight tremble.

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5. The Effect of the Arrangement of Microstructures on Anisotropic Dewetting

Anisotropic wetting and dewetting are very important properties on patterned surfaces that have recently attracted much interest.[25] In plants, it is well known that a water droplet can roll freely in all directions on the surface of a lotus leaf. However, we recently found an anisotropic dewetting tendency on the surface of a rice leaf.[26] It is considered that the arrangement of micropapillae on this surface could influence the motions of water droplets. Figure 4a shows a large-scale SEM image of the surface of a rice leaf (the inset is a HRSEM image of an individual papilla), which has micro- and nanostructures similar to those of the lotus leaf. The papilla are arranged in one-dimensional order parallel to the leaf edge (direction of arrow) and randomly in the other directions (perpendicular to the arrow). The value of α was different for water rolling along the direction of the arrow (3°–5°) and perpendicular to the arrow (9°–15°). The TCL of the location of water droplets should be the main factor influencing α. On the surface of a rice leaf, TCL is influenced by the micropapillae arrangement. In comparison, TCL is similar in all directions for the homogeneous and random distribution of micropapillae on the surface of a lotus leaf. These results offered important information for designing for controllable wettability on a solid surface. Accordingly, we prepared the rice-like ACNT films shown in Figure 4b. The ordered pattern of these films was in two dimensions with different spacings. The water droplets rolled readily across the larger spacings (along arrow direction). Other types of pattern can also be obtained as desired. A lateral micro- and nanostructure surface can be fabricated by local growth of packed ACNTs. In this way, we can prepare a useful patterned surface by tuning the parameters, which makes the building of super-hydrophobic nanochannels possible.

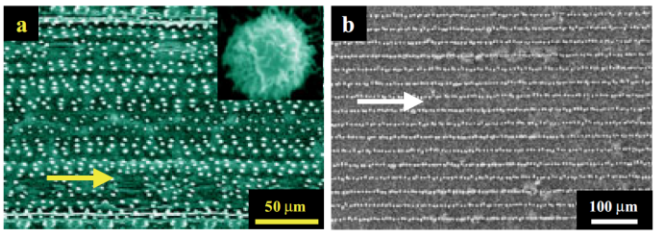

Fig. 4. a) Large-scale SEM images of the surface of a rice leaf (*Oryza sativa*) with different magnifications. b) SEM image of the top view of a rice-like ACNT film.

6. Conclusion

This paper gives a brief review of recent progress in super-hydrophobic surfaces. Studies of the surface of plant leaves provide a novel approach to constructing super-hydrophobic surfaces as in the natural world. Nanostructures are essential in fabricating super-hydrophobic surfaces with high CA, and multiscale structures can effectively reduce α of water droplets. Moreover, the arrangement of micro-array structures can influence how water droplets tend to move on these surfaces. Further efforts should concentrate on the application of super-hydrophobic surfaces to textiles,[27] coatings,[28] gene delivery,[29] microfluidic channels,[30] and non-wetting liquid transfer.[31]

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