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# Is a sliding layer formed when gliding on ice or snow? A chronological overview - as time-specific knowledge. Part I

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«God made the bulk; the surface was invented by the devil.»
Wolfgang Ernst Pauli (1900-1958), Austrian-Swiss physicist [1]

## Abstract

The fact that ice is slippery will have been experienced by the first people who stood and moved on it. Thousands of years ago, the Sami exploited this special property to be able to move with less energy. To understand the basic processes of friction, people like da Vinci, Euler, Amontons and Coulomb made important scientific contributions. These determined further advances in the surface structure of ice, snow, and water. The cause of icy slipperiness, entirely without pressure or friction, was first mentioned by Faraday in 1850 and explained in 1857 and as liquid water on the surface of ice. And Reynolds confirmed this slipperiness without pressure or friction in 1899. A surface layer on ice was described by Röntgen as a combination of two different molecular structures. With the technical development, a wide variety of new measuring methods were used to characterize the thickness, range, and properties of this special layer on the surface of ice - and referred to with a wide variety of terms. For every chemist it is trivial that the molecular structure of the surface of ice must be physically and chemically different from its interior: The molecules on the surfaces, faces, edges, corners, are bound only in three, two, or one spatial direction, as opposed to the interior with four bonds. A theoretical prerequisite was Pauling's finding that the molecule water, which is stable in itself, can combine with hydrogen bonds to form larger structures. All over the world, people have gone astray scientifically with various structures of water with the polywater, which in retrospect turned out to be an impurity. Thickness and properties of the slippery surface layer were determined with increasingly specific measuring methods, but also with most different measured values and their interpretations. Thus, many hypotheses have been published today. The most important findings to date concern the temperature limits, viscosity, density, and hydrophilicity of the water clusters on the surface. The sliding layer on ice or snow is a sliding on «water polymers» down to very low temperatures. The influence of a gliding surface with the surface of ice, snow or water is not the subject of this work.

# Introduction

Water cannot be used as a good lubricant because it has a low coefficient of viscosity. But in combination with lipid layers, water has a small coefficient of friction in biology for joint lubrication [2,3]. In nano dimensions water also acts with its three-dimensional hydrogen-bond network as a lubricant for molecular machines [4]. Therefore, it is surprising that surfaces of ice with pure water have very small coefficients of friction [5]. Ice has properties to form macromolecular structures with self-assembly and self-healing [6]. If you use E-Indigo [7,8], a chemically completely new, very good glide-layer for skis or sleds, you also must deal with ice and snow on which this winter sports equipment glides. Used waxes made of paraffines, greases, resins, graphite (graphene), PFC, siloxanes, gallium, molybdenum, and other disulfides, as well as nanoparticles are adapted as sliding layers for different snow conditions as mixtures. The experience with such waxes is very large, but less so the optimal surface roughness. For our innovation E-Indigo (Isantin$^{TM}$) as a glide coating, only years of experience are available to optimally adapt the interaction of the surfaces of ice and snow. It therefore makes sense to chronologically retrace and process the experiments accessible today and their interpretations for friction-layer on ice, snow, and water, to make improvements based on chemical findings. Whenever appropriate and possible, the verbatim statements of the researchers are used in the individual sections.

# Chronological overview

Years 2800 BC until 1900.

## 2800 BC

Johannes Schefferus (1621-1679) [10] describes that the Sámi people (approx. 2500 BC) used a thin, water-insoluble layer of tree resins or pitch on broad planks extremely smooth ski sole to massively reduce friction when gliding on wooden skis on snow. This innovation basically shows that a hydrophilic surface of wood slides worse on snow than the same surface with a hydrophobic coating. It can be assumed that the roughness of the gliding surface has already been considered, since improvements in gliding are immediately noticeable. These findings were fundamental for gliding contacts with snow because they achieved a smooth surface with a simultaneous reduction in wettability.

Figure 1: A sámi man on skis [9].

## 2000 BC

Gliding over the snow on skis or sleds has been known for thousands of years and recorded in rock carvings in Norway. These people must have thought about how long the skis had to be so that gliding over snow was possible with as little effort as possible - whether the rock carving shows the right proportions? Attention was also certainly paid to the finishing of the sliding surface, because here improvements were immediately noticeable as the force required for running. The use of skis is not a matter of course, because in other but similarly snowy areas the Eskimo did not use skis, but snowshoes when hunting, even the name derives from it: Eskimo: Ayisiniwok-Word: aayaskimeew = snowshoe netters [12].

Figure 2: The Rødøy skier - rock carving from 2000 BC - Rødøy, Nordland, Norway [11].

## 1509

Leonardo da Vinci (1452-1519) [14] made the first systematic study of friction. In his notes and sketches, dating from 1506-1508 Leonardo first visualizes the laws of friction. From these drawings and notes in his notebooks emerge three notable observations by da Vinci, which were followed by further developments of the laws of friction [15]:

1. The friction is independent of the apparent contact area,

2. the frictional resistance is directly proportional to the applied load,

3. friction has a constant value, which is now expressed as the coefficient of friction.

He then showed that he had repeatedly applied his findings to various mechanical problems for more than 20 years.

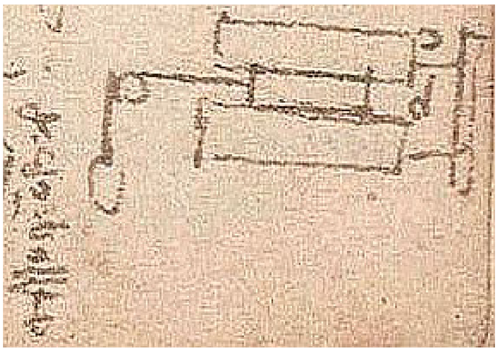

Figure 3: Leonardo da Vinci's experiments with friction underpinned the modern science of Tribology [13].

## 1557

Li J. *et al.*, [16] explain the transport of a large stone in Beijing (China) measuring 9.6 × 3.2 × 1.6 m (≈ 123 tons) over 70 km to the Forbidden City in 28 days in 1557 by a sledge pulled by men. It is briefly mentioned that the Large Stone Carving was transported to the site in deep winter with sledges sliding on an artificial ice path. The question is: Why was a sled still used when large-wheeled vehicles had been well developed in China for some 2,000 years? However, it can be proven that the sliding of wood on ice is more reliable and efficient than other lubricants. To allow easy gliding, it was important to pour water on the ice contact surface to make this type of transport possible.

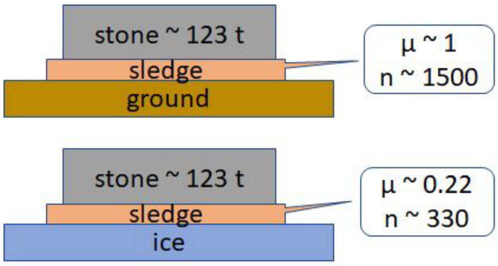


Figure 4: Estimated of the number of men n needed to pull a sledge with a 123-ton stone corresponding to two coefficients of the friction $\mu$.

## 1611

Johannes Kepler (1571-1631) [17] noted that each snowflake is a unique structure of hexagonal shape. He correctly assumed that their hexagonal shape comes from the cold but could not yet justify it physically.

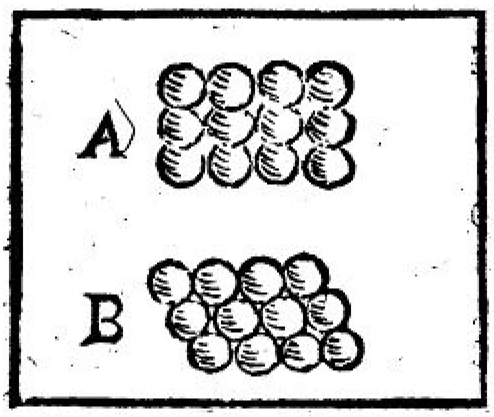


Figure 5: Arrangement A leads to rectangular, B to hexagonal structures (original from Kepler, p.9).

## 1612

Galileo Galilei (1564-1642) [18] argued that ice floats on the water because it has more vacuum and not less heat than the liquid. In this point he was right. This vacuum plays an important role in the peculiarities of the liquid water and the structure of the solid ice.

Figure 6: Ice floating on water.

## 1699

Philippe de la Hire (1640-1718) [19,20] provided an explanation for his observations in 1699. As a comparison, he surmised that bodies in contact have soft, flexible areas (like wood) that act as tiny springs that deform under the load (now called asperity, unevenness of surface, roughness, ruggedness). In addition, this deformation of each of these springs is proportional to the load it supports and independent of the total surface area of the bodies. He thought similar arguments would apply if the regions were hard and inelastic (as in rocks). However, then the areas that interlock would either rub against each other and wear out or slide over one another when sliding. In all these cases, he argued, the force of friction is independent of the apparent contact area but depends solely on normal loading. To a very limited extent, this model can also be applied to friction on ice and snow.

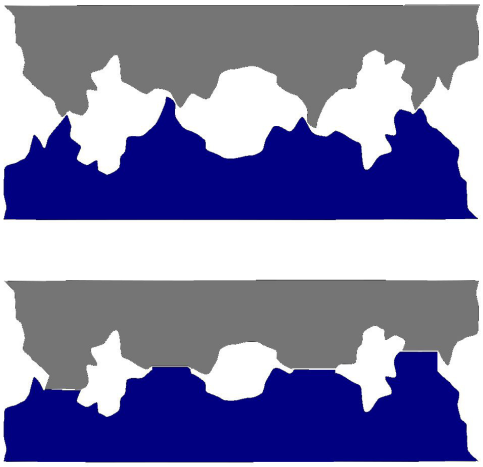

Figure 7: Roughness of unaltered (above) and abraded surface (below). Now defined as asperity, unevenness, roughness, ruggedness of surfaces.

Guillaume Amontons (1663-1705) [22,23,24] rediscovered the laws of friction established by Leonardo da Vinci. He published a study on static friction in 1699, which is considered, based on the theories of Philippe de la Hire, the first detailed scientific publication about these kinds of friction. For experimental investigations he designed a simple apparatus for testing static friction.

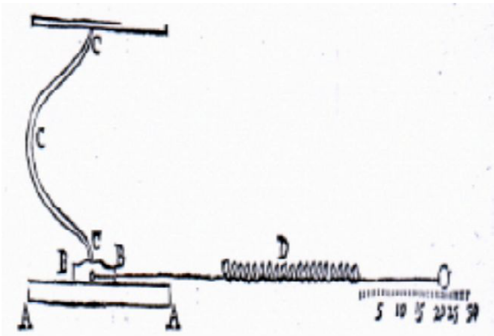

Figure 8: Amontons apparatus for measuring friction [20].

## 1748

Leonhard Euler (1707-1783) [26,27] distinguished between static friction and dynamic friction and theoretically analyzed the mechanism of sliding movement of a block on an inclined plane. For the frictional resistance, he adopted the model of rigidly interlocking asperities, like saw teeth, as the cause. From this he concluded that static friction is always greater than kinetic friction. This is a model for ideal, geometric surfaces, which is mathematically perfectly formulated.

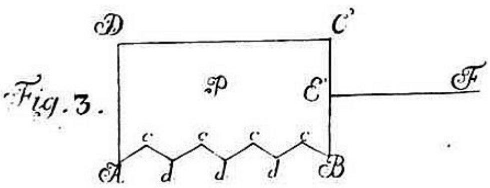

Figure 9: Eulers model of friction on a pair of interlocked saw tooth pattern surfaces where the force is calculated to surmount the asperities [25].

## 1809

Charles-Augustin de Coulomb [28], (1736-1806) devised a simple law of friction for the ratio of the normal force (weight force) and the force necessary to overcome friction for a solid on planar and inclined surfaces – the Coulomb law of friction. «... dans la première, nous chercherons le frottement des surfaces qui glissent l'une sur l'autre, tel que celui d'une surface qui glisse le long d'un plan incline. Static friction and sliding friction are also referred to together as Coulomb friction.» That any friction is intuitively associated with corrugation was the first explanation proposed by Coulomb.

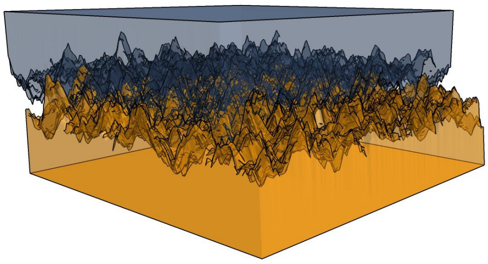

Figure 10: Simulated blocks with fractal rough surfaces, exhibiting static frictional interactions. (Figure: CaoHao, 2014, Wikipedia Public Domain)

## 1849-1857

William Thomson, Baron Kelvin (1824-1907) [29] and James Thomson (1822-1892) wrote [30]: «... water at the freezing point may be converted into ice by a process solely mechanical, and yet without the final expenditure of any mechanical work» and further in this work [31]: «The following is the rationale by which these conclusions are proved.» He added: « While the water was freezing and under a pressure greater than that of the atmosphere, its temperature was below 0 °C. That is, the freezing point of water under the pressure of one additional atmosphere is -0.0075 °C; and therefore, denoting the pressure above an atmosphere in atmospheres as units with n, one obtains t, the freezing point depression in degrees Celsius, according to the following formula -t = 0.0075 n.» (1 atm = 101.325 kPa = 1 bar).

In a follow-up work, the changed ice surface is referred to as liquid water. And in an 1857 addendum he wrote [32]: «I have proposed - namely, the lowering of the freezing or melting point by pressure and the fact that ice cannot exist at 0° Celsius under a pressure exceeding that of the atmosphere.»

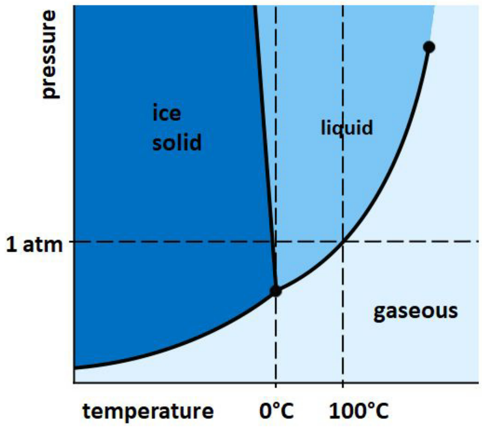


Figure 11: Phase diagram of water as a function of temperature and pressure.

## 1850, 1859

Michael Faraday (1791-1867) [33] postulated in 1859 that a thin film of liquid water covers the surface of ice - even at temperatures well below freezing: «Mr. Faraday then invited attention to the extraordinary property of ice in solidifying water which is in contact with it. Two pieces of moist ice will consolidate into one. Hence the property of damp snow to become compacted into a snowball an effect which cannot be produced on dry, hard-frozen snow. Mr. Faraday suggested, and illustrated by a diagram, that a film of water must possess the property of freezing when placed between two sets of icy particles, though it will not be affected by a single set of particles.» This cementation will take place in air, in a vacuum, or in water. Faraday published Research in Chemistry and Physics [34] «... still adheres to his original mode of accounting for the phenomenon he had observed, and for which he now adopts the name regelation.» Regelation is the phenomenon of ice melting under pressure and then refreezing once the pressure is released. Regelation only occurs for materials that expand upon freezing so that the melting point decreases as external pressure increases. For example, for 1 atm of pressure applied, the melting point of (water) ice falls by 0.0072 °C. Regelation also occurs in other materials, such as gallium and bismuth, but usually, a discussion of regelation pertains to water (new experiments see [35]).

Faraday first showed how entirely colouring matter, salts and alkalies are expelled in freezing [36]: «A solution of sulphate of indigo, diluted sulphuric acid, and diluted ammonia were partially frozen in glass test-tubes: as soon as the operation had been carried on long enough to produce an icy lining of each tube, the unfrozen liquid was poured out and the ice dislodged. This ice was found in every instance perfectly colourless, and, when dissolved, perfectly free from acid or alkali, although the unfrozen liquid exhibited in the first experiment a more intense blue colour, in the second a stronger acid, and in the third a more powerful alkaline reaction than the liquor which was put into the freezing mixture.»

«All our theories and explanations of the laws which govern them, whether particular or general, are necessarily deduced from insufficient data.» [37]

Michael Faraday (1791-1867), British scientist who began his career as a chemist

Figure 12: Pieces of ice stick together on light contact.

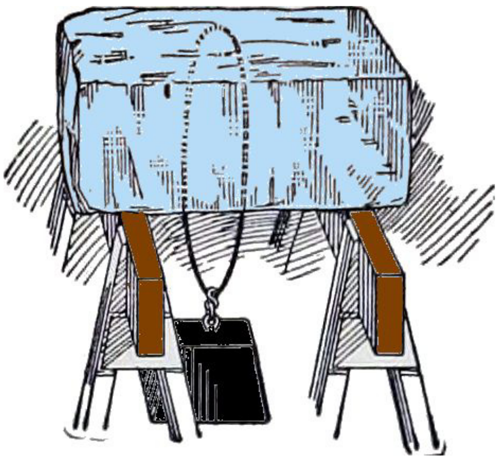

Figure 13: Regelation: An iron wire with weights melts through a block of ice without breaking it. (Figure adapted from Wikipedia Public Domain)

Figure 14: Exclusion of dissolved substances when water freezes (left: water with dissolved blue indigo carmine, right: ice of the solution of indigo carmine).

Figure 15: Insoluble indigo is excluded when freezing an aqueous dispersion (d $\approx$ 1 $\mu$m) due to its higher density on the ground.

## 1859

John Tyndall (1820-1893) [38] differentiated, with good observations between the properties of particles that are on the surface of ice and those that make up the solid: «Now as regards the amount of motion necessary to produce this liberty of liquidity, the particles at the surface of a mass of ice must be very differently circumstanced from those in the interior, which are influenced and controlled on every side by other particles.» (see also [39]). He argued: «The foregoing considerations show that liquefaction takes place at the surface of a mass of ice at a lower temperature than that required to liquefy the interior of the solid. Before being brought together, the surfaces had the motion of liquidity, but the interior of the ice has not this motion; and as equilibrium will soon set in between the masses on each side of the liquid film and the film itself, the film will be reduced to a state of motion inconsistent with liquidity. In other words, it becomes frozen and cements the two surfaces of ice between which it is enclosed.»

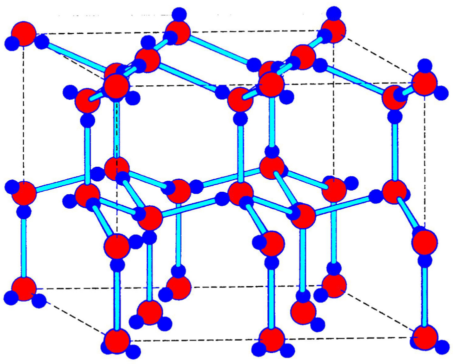

Figure 16: Particles, which are water molecules, behave differently on the surface compared to the interior of ice because they have parts open to the environment.

## 1864

Ludwig Ferdinand Wilhelmy (1812-1864) [40] concludes from his experiments: «If we immerse a solid body in a chemically pure, consequently identical liquid, depending on the properties of both, a more or less large compression of the liquid takes place on the surface of the former.» And further conclusions: The water layer thickness on glass was calculated as 3.5 $\mu$m (mean). «If we immerse a solid body in a chemically pure, and consequently completely identical, liquid, the liquid on the surface of the former will be compressed to a greater or lesser extent, depending on the nature of both.»

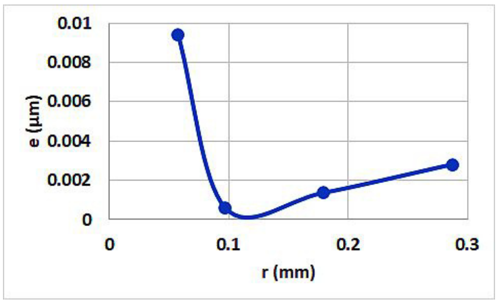


Figure 17: Water layer thickness (e) in a glass capillary with radius (r). (Data from Wilhelmy)

## 1886

Osborne Reynolds (1842-1912) [41] speaking for himself: «... ice was slippery when I was born, I never knew it otherwise, and, to put it shortly, it was slippery because it was ice, whereas it now seems to me that, of all the secrets nature has concealed by her method of deadening curiosity by leaving them exposed, in this her method has been the most successful.» His observation: «I notice that without great care you cannot walk on ice at $31\frac{1}{2}°$ (-0.3 °C) in leather boots without nails, whereas you can walk safely with boots with somewhat blunt nails under the same circumstances; with a temperature of 27° (-2.8 °C) you can walk with leather boots almost as safely as on any polished floor, while with somewhat blunt nails it is very unsafe to walk on uneven ice.» The consequence of this observation is that ice is slippery even without friction and pressure.

His findings are further: «Now water had, at the time, not been recognized as a lubricant; its viscosity is from 200 to 400 times less than oil, but from my research it appeared that it is a lubricant in proportion to its viscosity.» (For temperatures over the range from -10 to -30 °C see also [42]). «On ice near 32° (0 °C) skaters find no resistance however slowly they may move, while on hard ice it is necessary to move quickly, or the skates seize, showing that the ice melts under the edge, but owing to the small area of the lubricating surface, the lubricant is squeezed out rapidly, thus destroying the lubrication below certain speeds, as in Mr. Tower's experiment.» «Ice is not the only slippery thing in the world, but it is the only one of all the solid substances which, in the condition nature has left them on the surface of the earth, possesses the property of perfect slipperiness.» «The other sources of perfect slipperiness are complex; a smooth solid surface covered by a viscous fluid, as a well-greased board, is perfectly slippery just as ice is, which fact had been taken for granted much in the same way as the slipperiness of ice, neither more nor less.»

Wilson Alwyn Bentley (1865-1931) [44,45,46], also known as Snowflake Bentley, was the first known person to take detailed photographs of snowflakes, beginning in 1890.

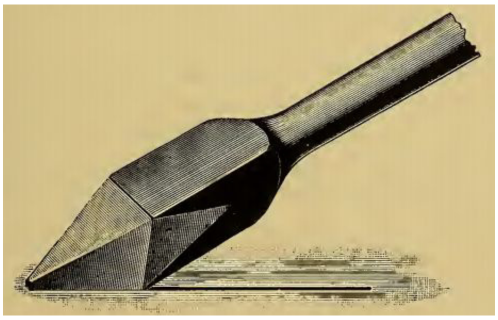

Figure 18: With the accident to see if the soldering-iron was hot enough to melt the solder instantly led to the analogy to the skate: «I had never before thought of considering why ice was slippery.»(Figure: the original publication)

Figure 19: Ice is slippery without pressure or friction.

## 1890-1938

Nakaya, U. *et al.* [47] measured at the temperature of -15.3 °C to -16 °C: «The rate of growth of the ray of a crystal in dendritic form varies considerably with the condition of formation but usually it can be taken as nearly 0.05 mm/min.» The snowflakes grow as water in the form of vapor binds to form ice on the surface.

An average human hair is about 0.05 to 0.08 mm thick, and it was found that an ice crystal of granular shape had grown on the thread with the same extension, with a knob as the core [48].

Today, the process of snow crystal formation would be called self-organization for macromolecular structures (see also Kepler 1611).

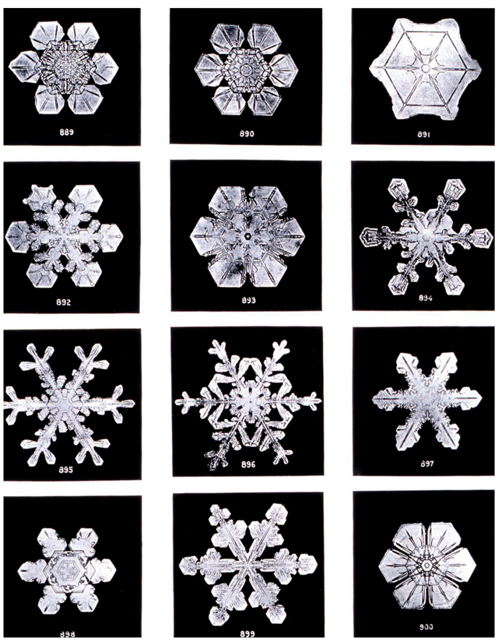

Figure 20: Snowflakes microphotographed by Wilson A. Bentley in 1890 and published in the book "Snow Crystals" in 1931 [43].

## 1892

Wilhelm Conrad Röntgen (1845-1923) [49] sought explanations for the following well-known phenomena of water:

1. It is densest in the liquid state at 4 °C rather than becoming steadily denser as it cools.

2. That the compressibility of water in the temperature interval from 0 to 50 °C decreases with increasing temperature.

3. That the average coefficient of expansion of water between 0 °C and 50 °C up to pressures of 2500-3000 atmospheres increases continuously with the pressure, and the more rapidly the lower the temperature and the smaller the pressure.

4. That the viscosity of water of approx. 18 °C is reduced by pressure, i.e., it becomes thinner.

He found an explanation in the assumption that liquid water consists of an aggregate of two types of differently constituted molecules: of variable proportions of water molecules with ice molecules as clusters dissolved in them. The proportions affected by temperature and pressure determine the corresponding properties (a quite modern view [50]).

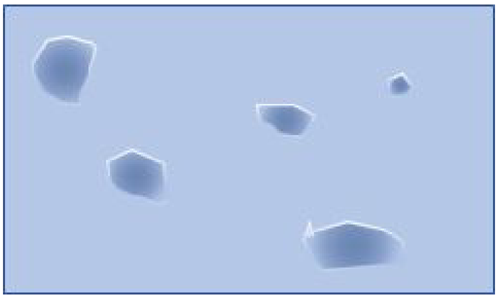

Figure 21: Liquid water and ice consist of water- and ice-molecules in different proportions, depending on its temperature.

## 1899

John Joly (1857-1933) [51] published: «The pressure under the edge of a skate is very great. The blade touches for a short length of the hog-back curve, and, in the case of smooth ice, along a line of indefinite thinness, so that until the skate has penetrated some distance into the ice the pressure obtaining is great; in the first instance, theoretically infinite. But this pressure involves the liquefaction, to some extent, of the ice beneath the skate, and penetration or 'bite' follows as a matter of course. As the blade sinks, an area is reached at which the pressure is inoperative, i.e., inadequate to reduce the melting-point below the temperature of the surroundings. Thus, estimating the pressure for that position of the edge when the bearing area has become 1/50 of a square inch, and assuming the weight of the skater as 140 lbs., and also that no other forces act to urge the blade, we find a pressure of 7000 lbs. to the square inch (48'263'300 N/m$^2$), sufficient to ensure the melting of the ice at ≈-3.5 °C. With very cold ice, the pressure will rapidly attain the inoperative intensity, so that it will be found difficult to obtain 'bite' - a state of things skaters are familiar with. But it would appear that some penetration must ensue. On very cold ice, 'hollow-ground' skates will have the advantage.»

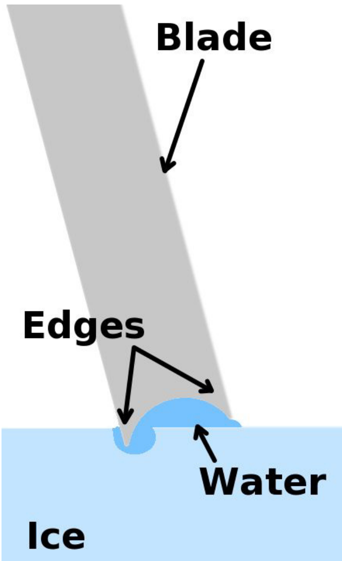


Figure 22: Cross section of the 'hollow-ground' blade of an ice skate.

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