Physical Properties of Ice: Microstructure, Bulk Properties, and Molecular Behavior

ESS431: Principles of Glaciology

ESS505: The Cryosphere

Wednesday, 10/03 – Knut Christianson

Today's Questions:

- What is the molecular structure (physical arrangement of atoms & molecules) of water as a vapor, as a liquid, and as a gas?

- How are the molecular (microscopic) properties and bulk (macroscopic) properties of ice related?

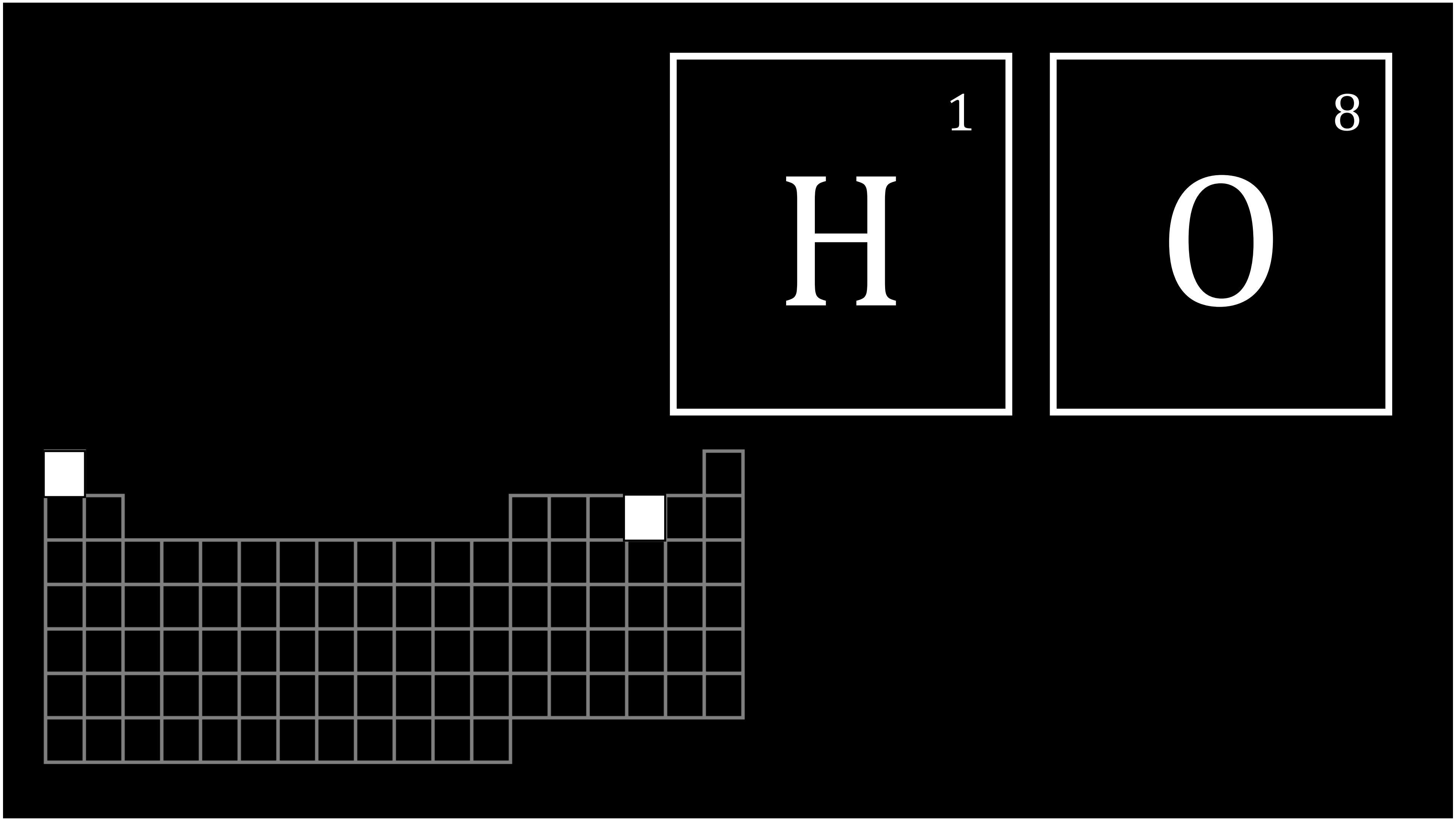
- What is "equilibrium vapor pressure"? How does this concept explain phase changes of water and snow grain metamorphism?

- What are the thermal properties (heat capacity, thermal conductivity, thermal volumetric properties) of water?

The Molecular and Crystal Structure of Ice

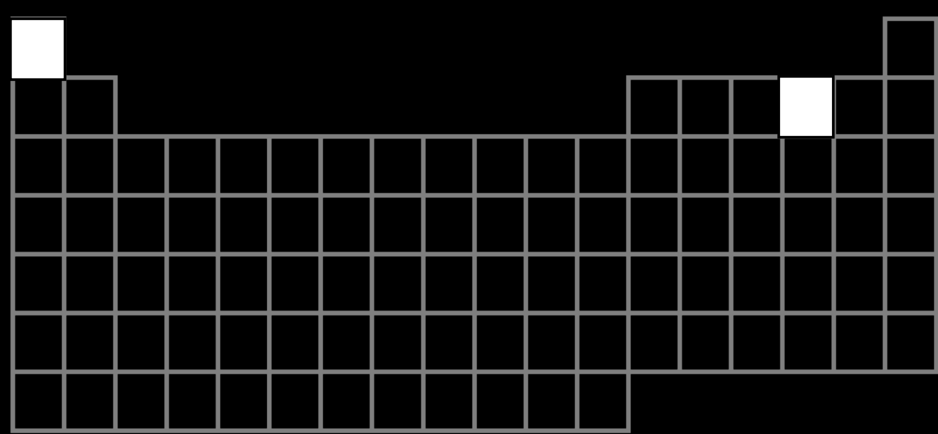
Thermodynamics of Bulk Properties of H_20

Relationship Between Molecular Properties and Bulk Properties


1
H
8
O

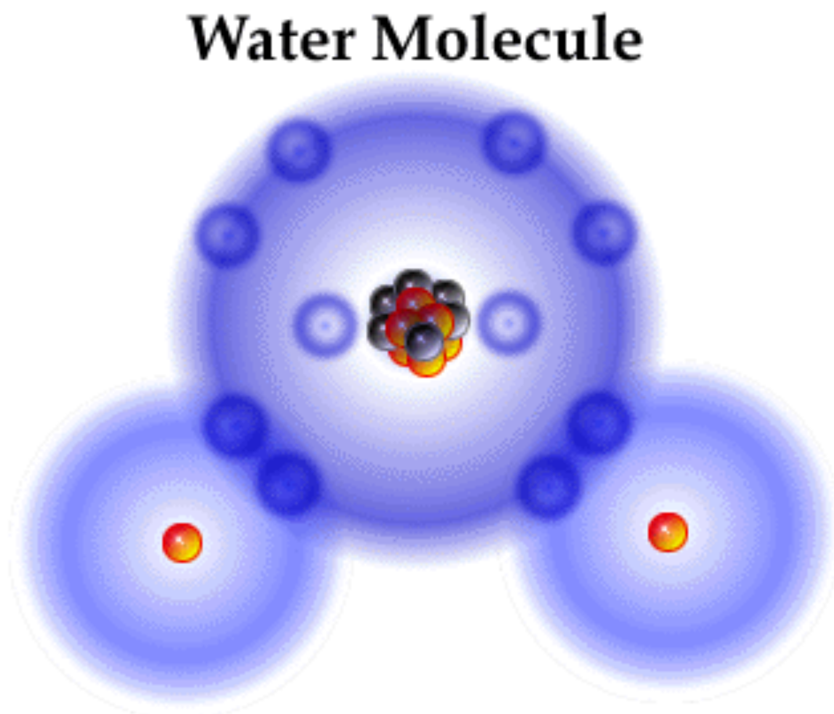
1
H

8
O



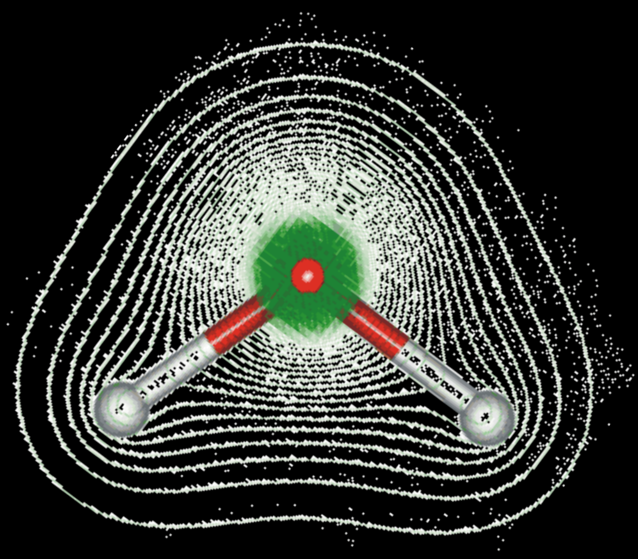
- Oxygen has 6 electrons in its valence shell
- Hydrogen bonds result in a polar molecule

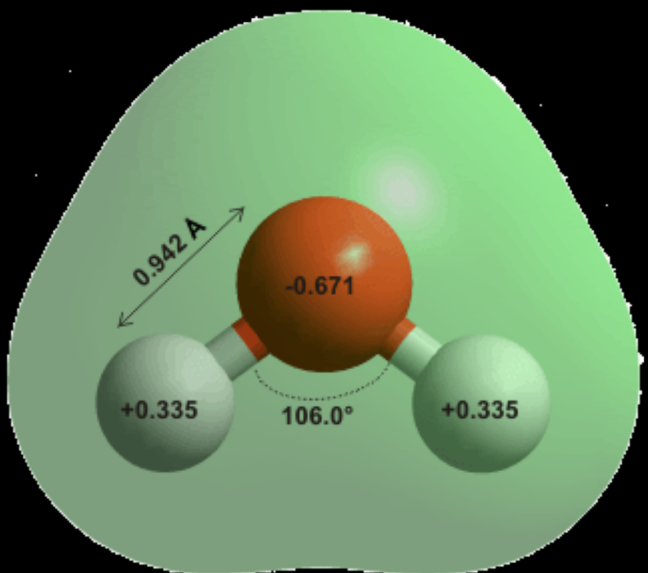
Tetrahedral Structure of H_2O Molecule



www.brooklyn.cuny.edu/bc/ahp/SDgraphics/PSgraphics/SD.PS.LG.Water.html

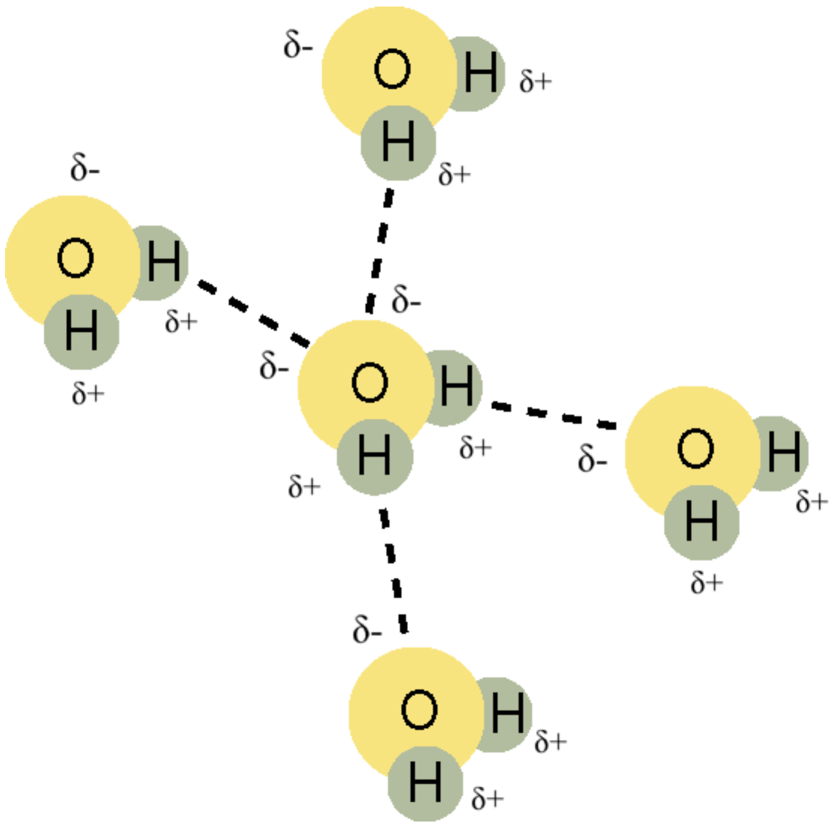
Tetrahedral Structure of H_2O Molecule: Orbital Hybridization

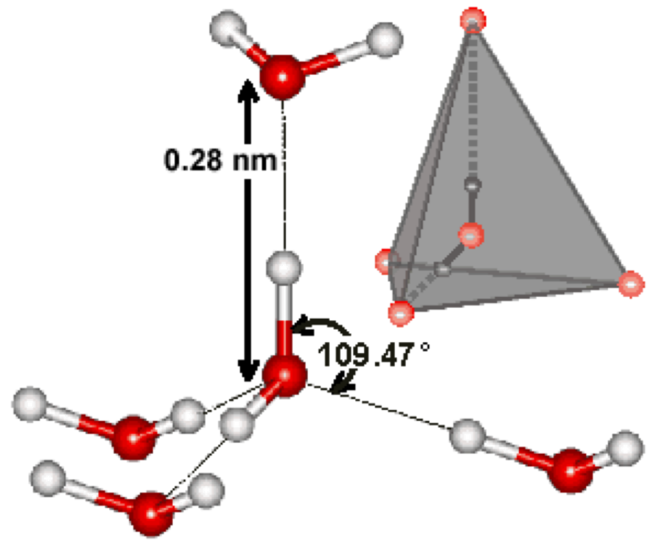




http://www1.lsbu.ac.uk/water/water_molecule.html

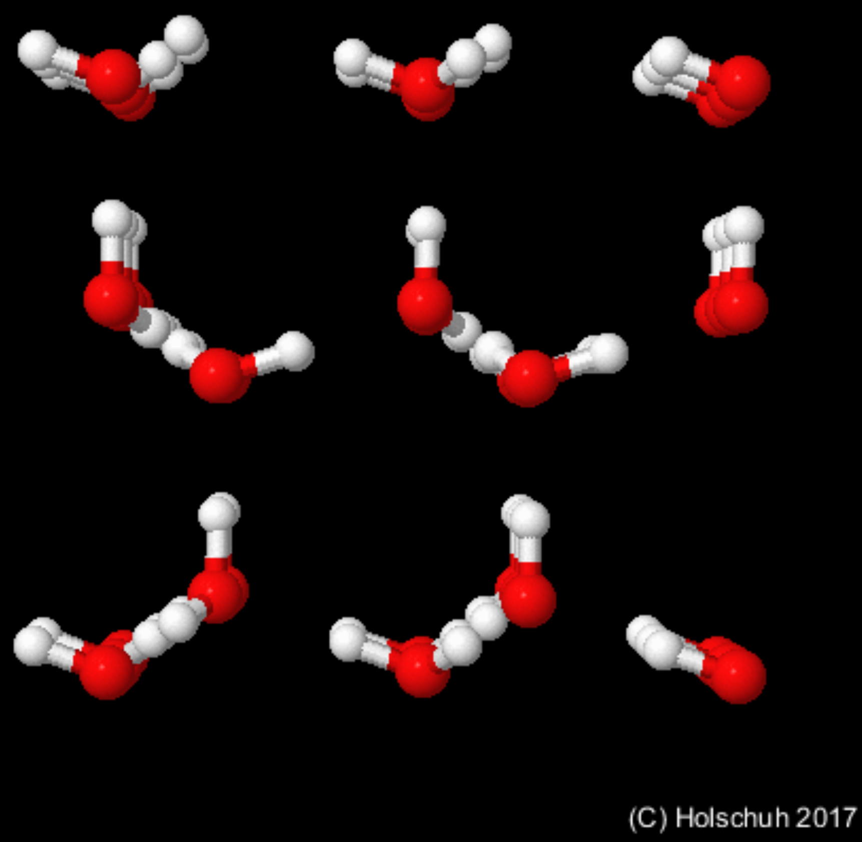
The Hydrogen Bond:
Intermediate Strength Electrostatic Bond



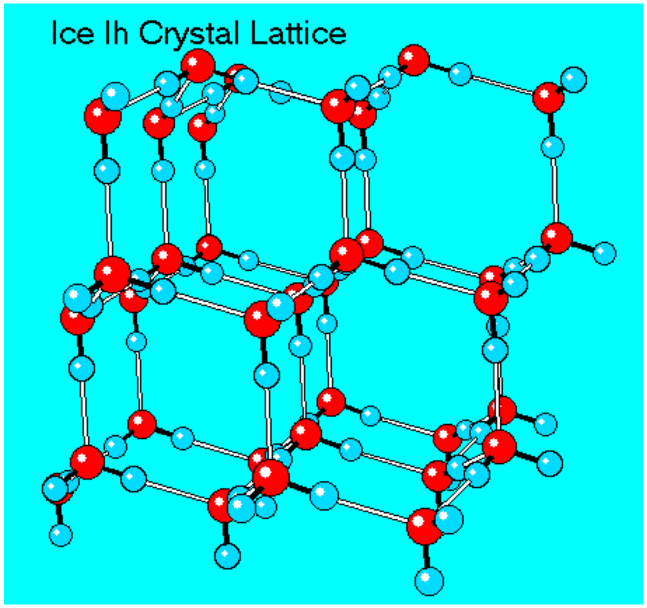


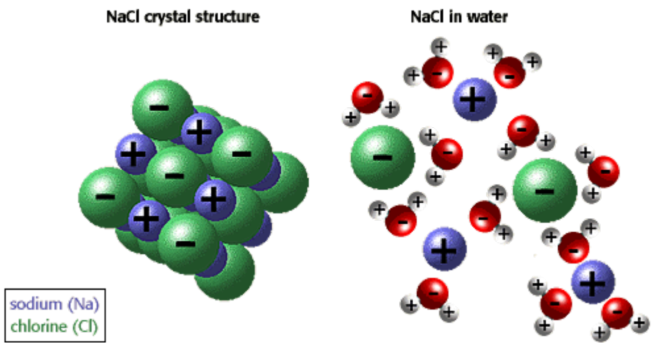
http://www1.lsbu.ac.uk/water/water_molecule.html
ed101.bu.edu/StudentDoc/Archives/spring04/srb2007/Site

- The primary form of ice on Earth is "Hexagonal Ice"
- Planes of hydrogen bonds form perpendicular to the "c-axis"
- These planes are mechanically weaker than other orientations of the molecule



Ice Lattice



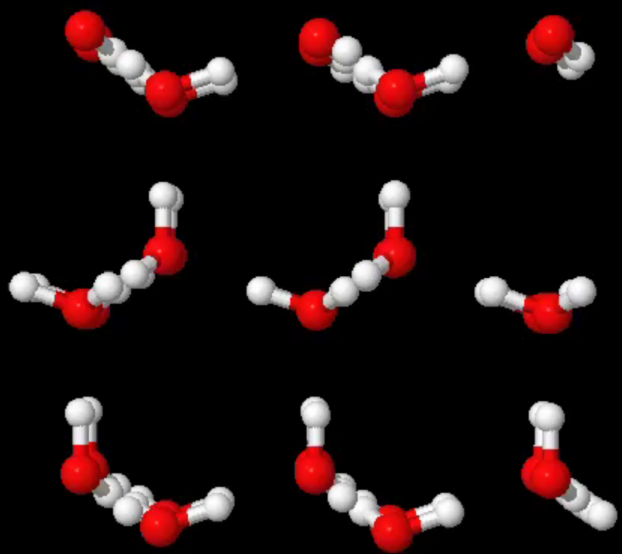


There is lots of empty space in the ice lattice.

http://www.its.caltech.edu/~atomic/snowcrystals/ice/ice.htm

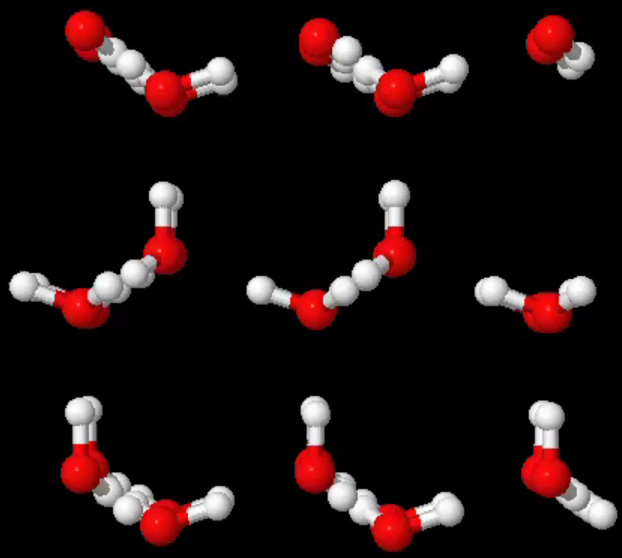
Proton Disorder

- Defects (2 or 0 protons on an H-bond) can move through the lattice.



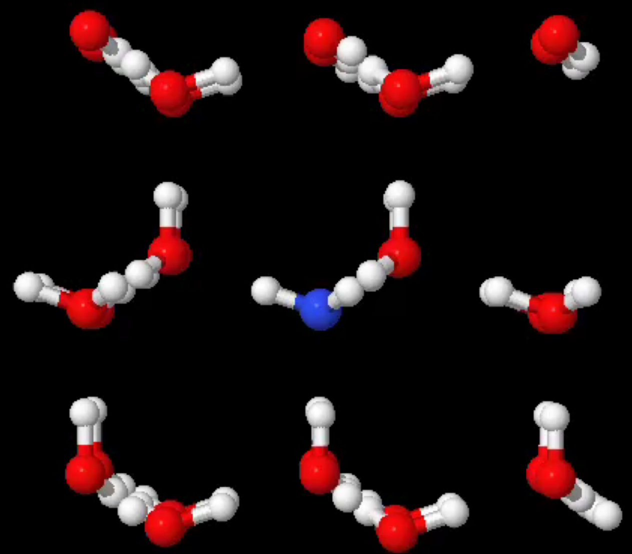
Proton Disorder

- Defects (2 or 0 protons on an H-bond) can move through the lattice.
- If there is an applied voltage, the motion is not random, i.e. becomes an electric current of positive charges



Proton Disorder

- Defects (2 or 0 protons on an H-bond) can move through the lattice.
- If there is an applied voltage, the motion is not random, i.e. becomes an electric current of positive charges
- Even at absolute zero, ice still has some entropy



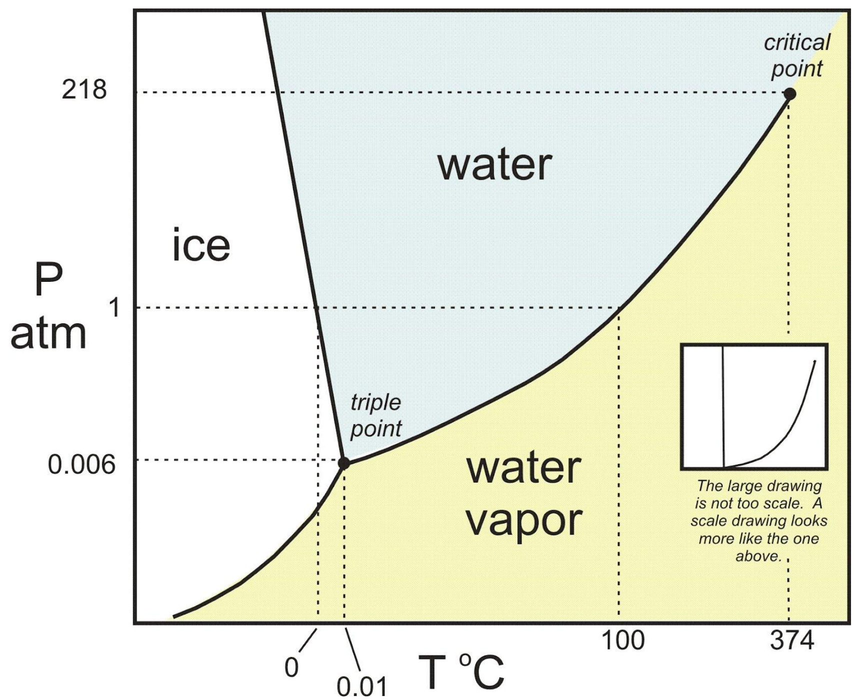
The Molecular and Crystal Structure of Ice

Thermodynamics of Bulk Properties of H20

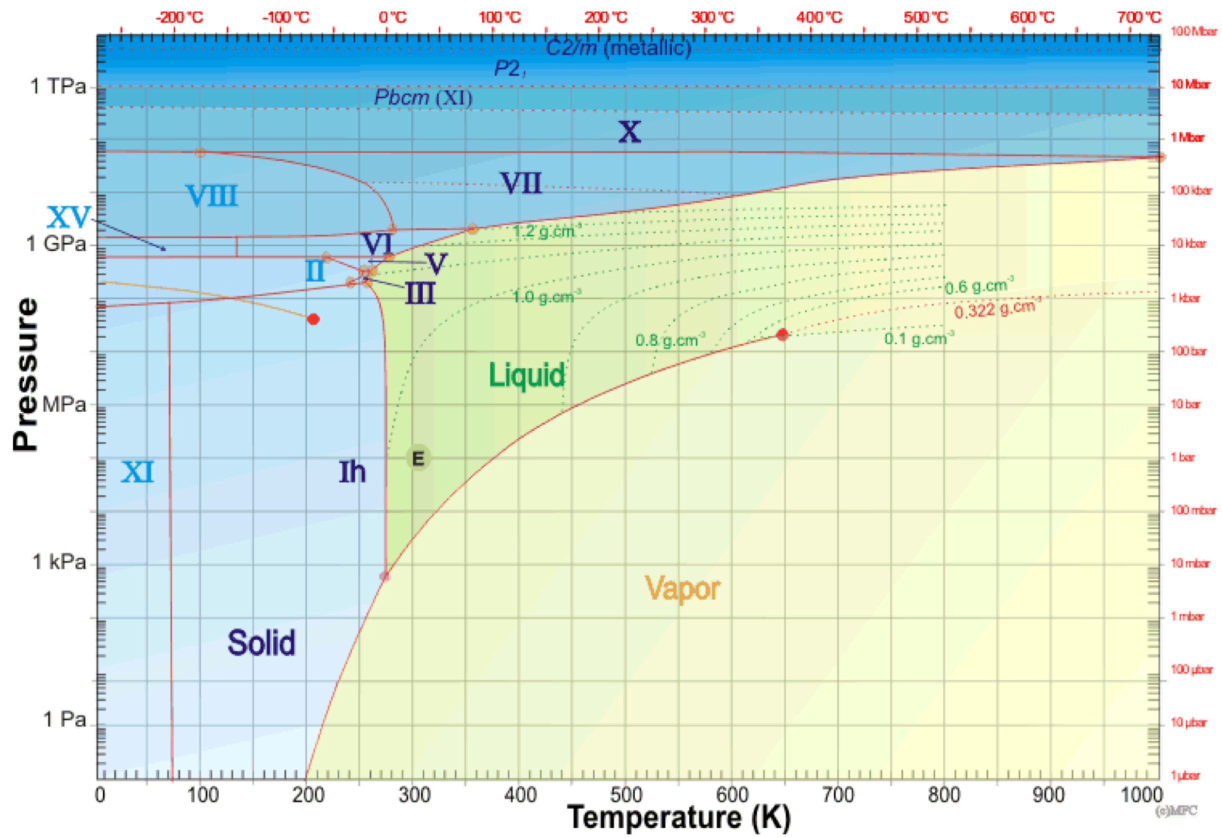
Relationship Between Molecular Properties and Bulk Properties

Why does H_2O change phase?

liquid-vapor	solid-liquid	solid-vapor

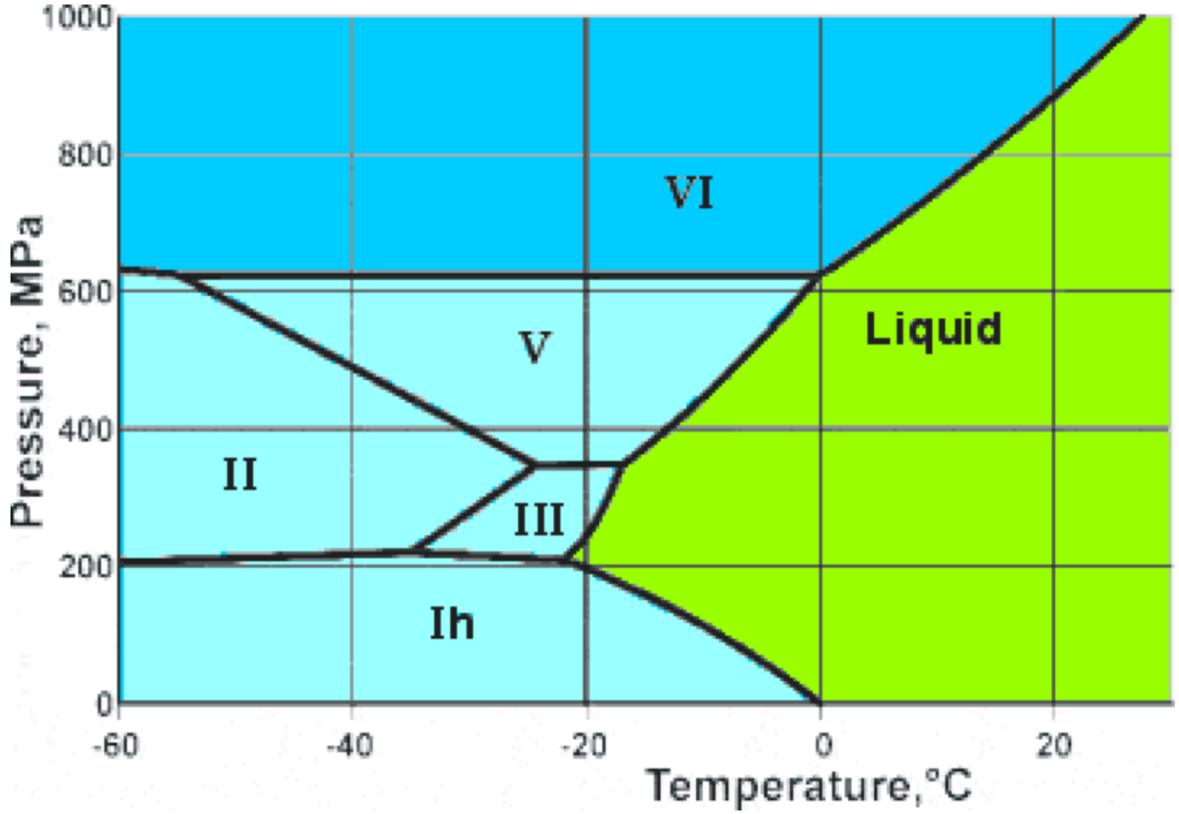


Phase Diagram for H_2O



http://www.lsbu.ac.uk/water/

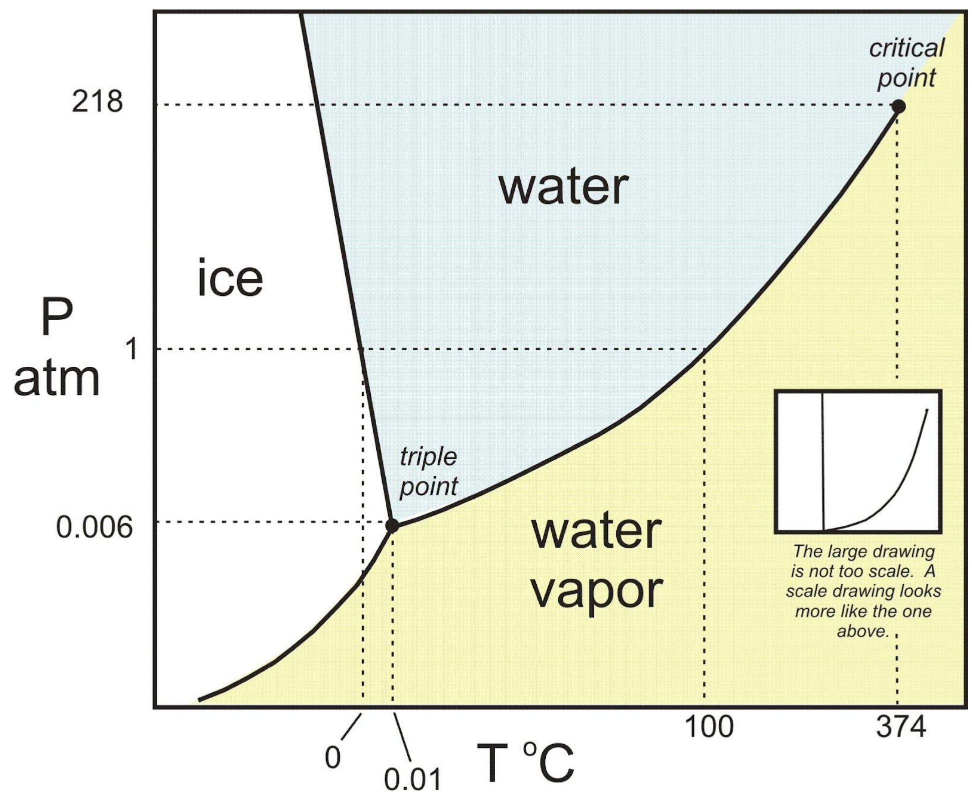
Detail near 10^8 Pa



http://www.lsbu.ac.uk/water/phase.html

Phase Diagram

- The phase diagram of water describes bulk properties, but not individual molecular behavior.

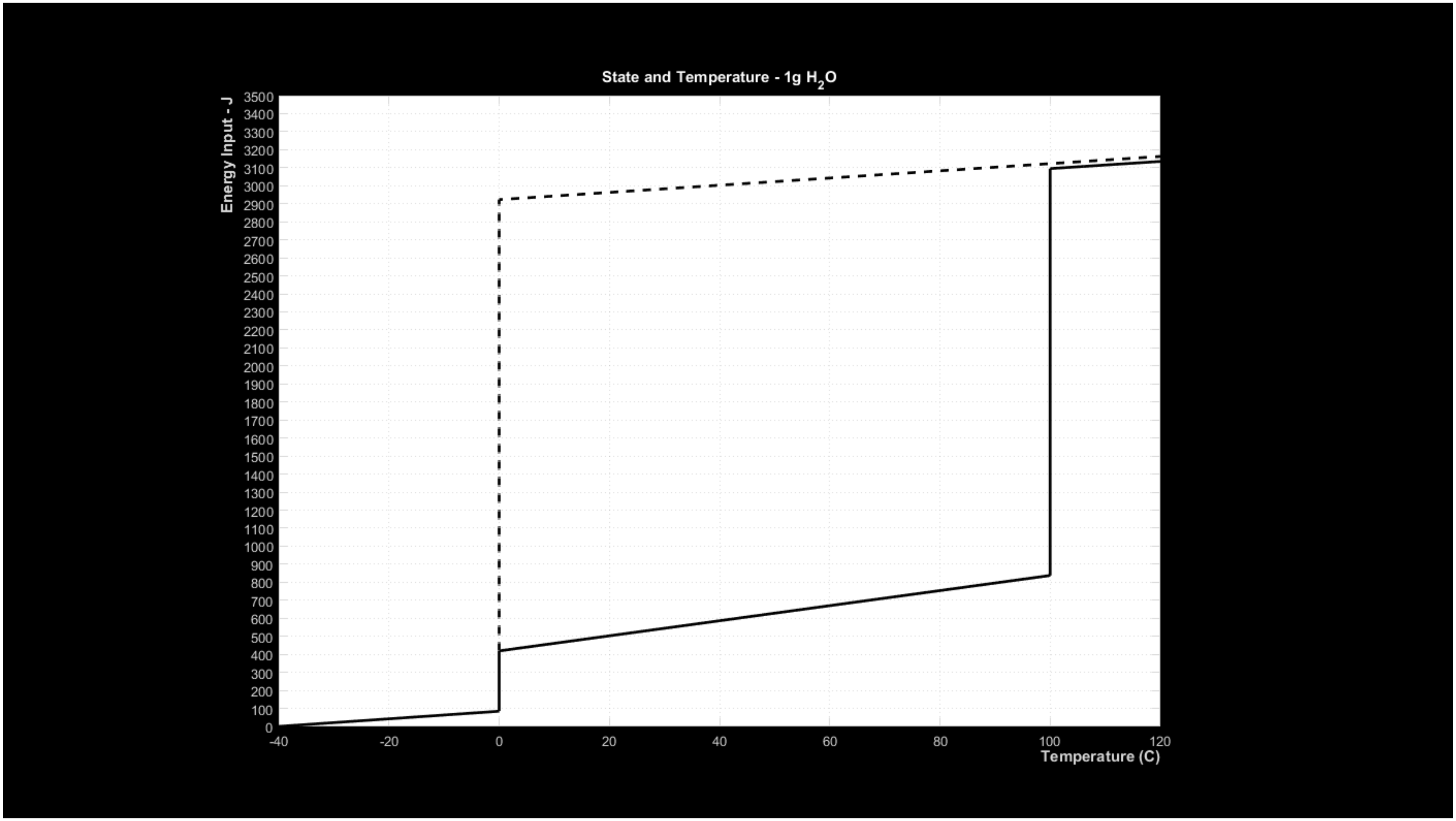


Bulk Properties of Note

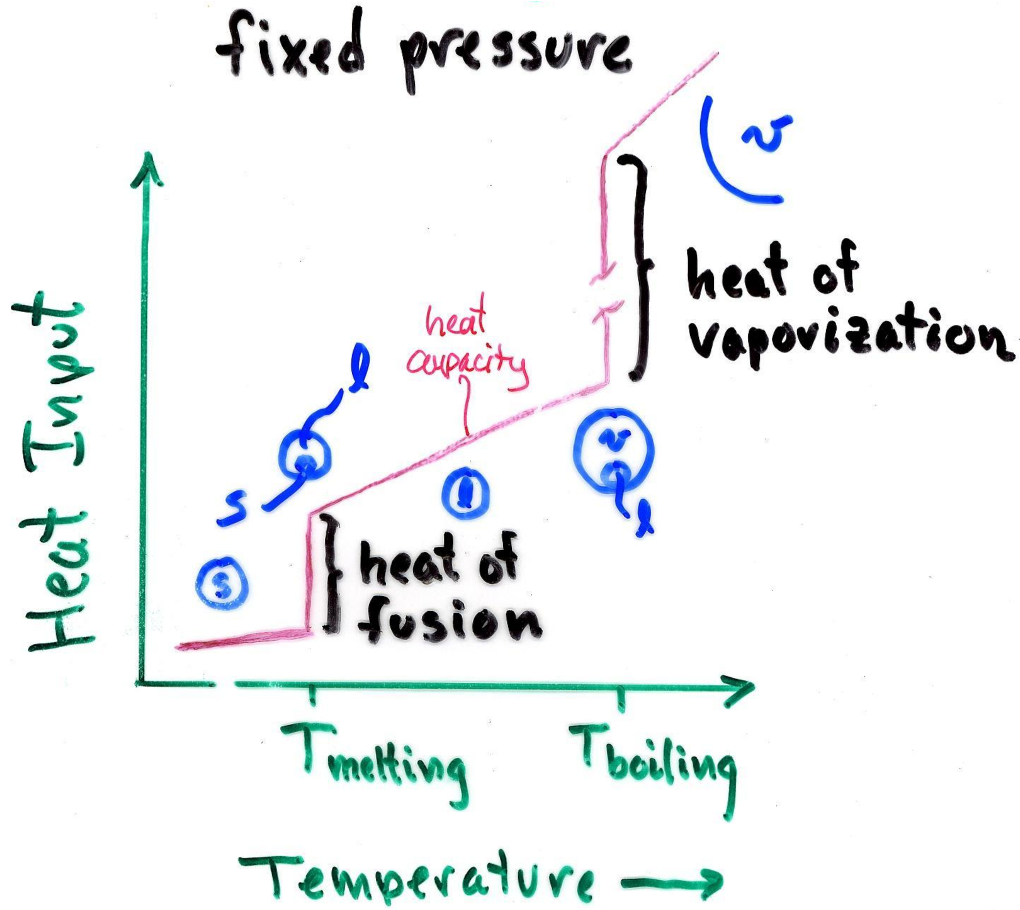
- **Latent Heat of Fusion:** Amount of energy required to change a substance state from solid to liquid, per unit mass.
- **Latent Heat of Vaporization:** Amount of energy required to change a substance state from liquid to gas, per unit mass.
- **Specific Heat Capacity:** Amount of energy required to raise the temperature of a substance, per unit mass.
- **Volumetric Changes:** Expansion/Contraction as function of phase change and temperature

Some Thermal Properties

Latent heat of fusion:		$334\ \text{kJ kg}^{-1}$
Latent heat of vaporization:		$2255\ \text{kJ kg}^{-1}$
Specific heat capacity:	ice	$2.1\ \text{kJ kg}^{-1}\ {}^{o}\text{C}^{-1}$
	water	4.18
Thermal conductivity:	ice	$2.3\ \text{W m}^{-1}\ {}^{o}\text{C}^{-1}$
	water	0.6
Thermal expansion coefficient:	ice	$5 \times 10^{-5}\ {}^{o}\text{C}^{-1}$
	water	$-6.6 \times 10^{-5}\ {}^{o}\text{C}^{-1}$ (at 0^{o}C)
		2.1×10^{-4} (at 20^{o}C)

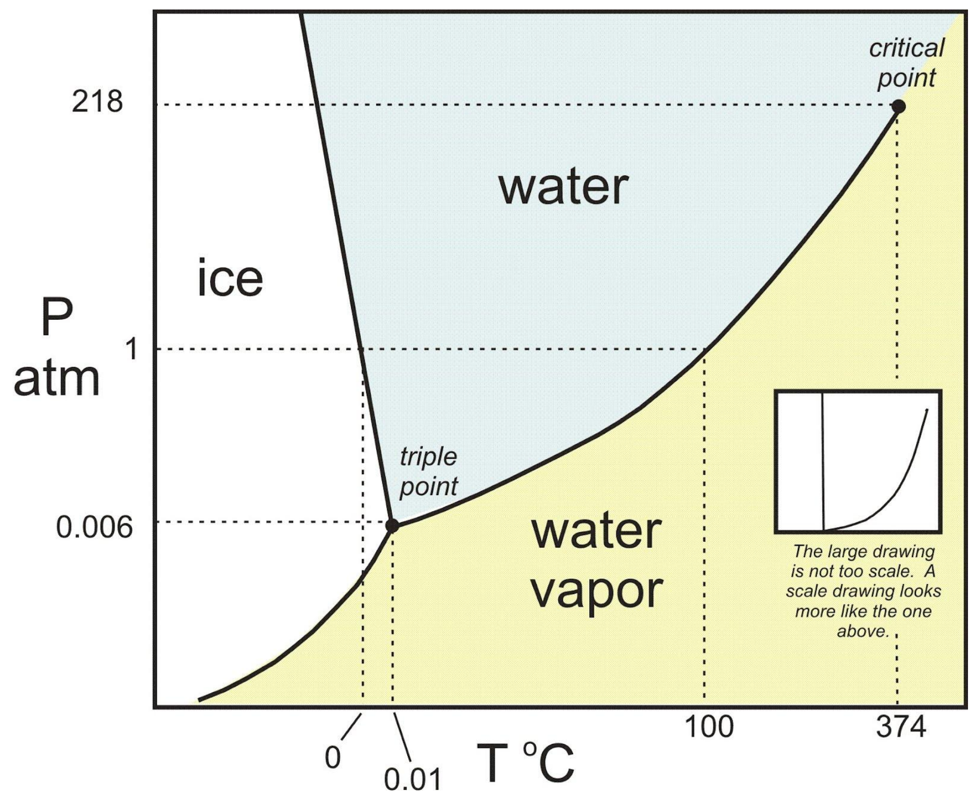

State and Temperature - 1g H2O
Energy Input - J
3500
3400
3300
3200
3100
3000
2900
2800
2700
2600
2500
2400
2300
2200
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-40
-20
0
20
40
60
80
100
120
Temperature (C)

Heating H_2O


fixed pressure
Heat Input
heat capacity
heat of vaporization
heat of fusion
s
l
v
Tmelting
Tboiling
Temperature →

Phase Diagram

- The phase diagram of water describes bulk properties, but not individual molecular behavior.



Hydrogen Bonds and Phase Changes

- It takes energy to break bonds (like springs)

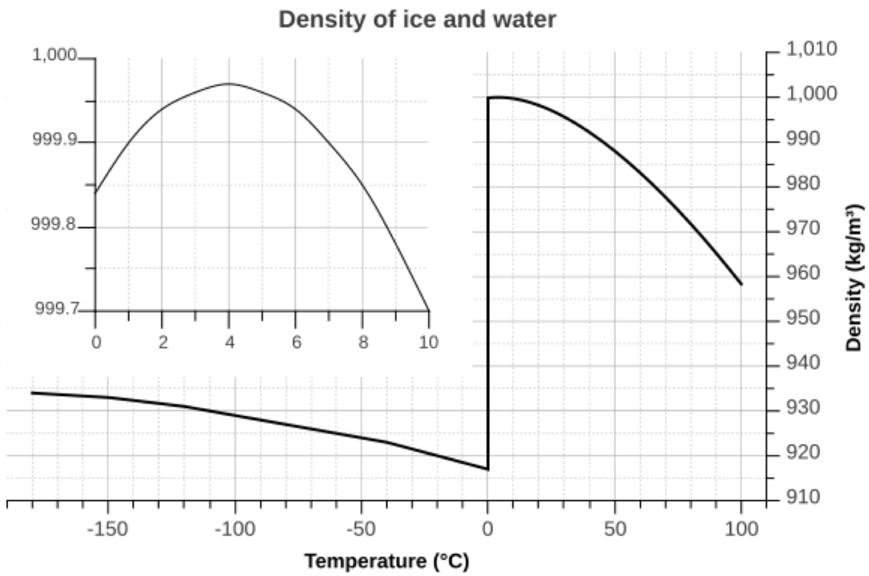
- To convert ice into liquid, we need to break ~15% of the hydrogen bonds

- To convert liquid water to vapor, we need to break the remaining 85% of the H-bonds

Heat of fusion (melting): 334 kJ kg^{-1}
Heat of vaporization (boiling): 2255 kJ kg^{-1}

$$\frac{334}{334 + 2255} \approx 13\%$$

Density of Water



- Why is water more dense than ice?
- Why is the maximum density at 4^{o}C?

The Molecular and Crystal Structure of Ice

Thermodynamics of Bulk Properties of H20

Relationship Between Molecular Properties and Bulk Properties

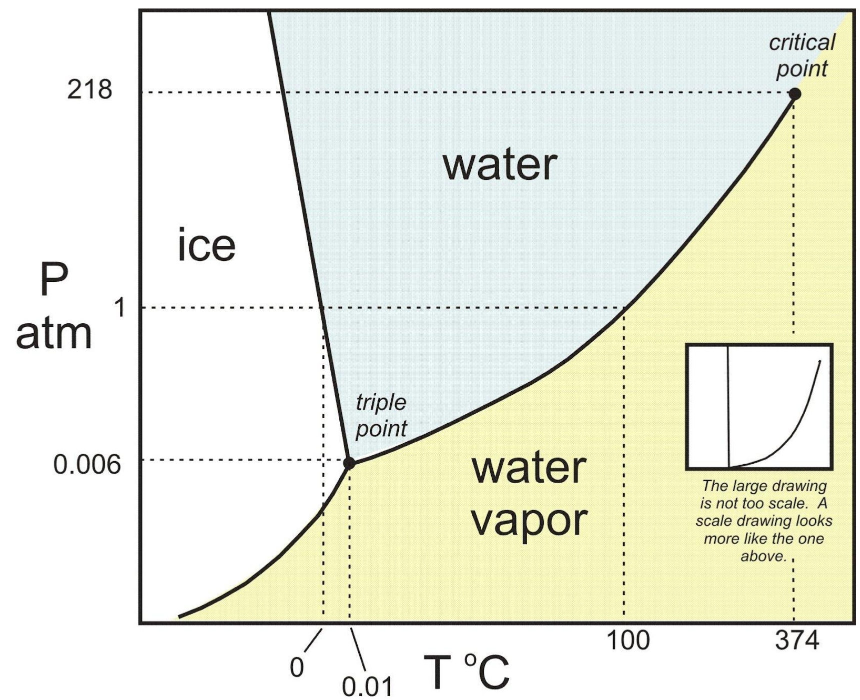
How does H_2O change with T and P?

liquid-vapor

solid-liquid

solid-vapor

- The phase diagram of water describes bulk properties, but not individual molecular behavior.



What is Temperature?

Energy is stored in various ways at molecular level:
- Kinetic energy (fast-moving molecules)
- Molecular rotations
- Bond oscillations (vibrating springs)
- Lattice vibrations (more springs)

Each different way is called a "degree of freedom".

Temperature measures amount of energy stored on average in ***each*** degree of freedom.

What is Heat Capacity?

Heat capacity measures amount of energy needed to raise temperature of 1 kg by 1 deg C.

We have to add energy equally to every degree of freedom (equipartition theorem).

- The more degrees of freedom in a substance, the higher its heat capacity will be.

Liquid water has a very high heat capacity.

What is Thermal Conductivity?

Thermal conductivity (K) measures the ease with which thermal energy can move through a substance (heat flux Q, in units of J m^{-2} s^{-1}) in response to a temperature gradient (dT/dx)

$$Q = K\, dT/dx$$

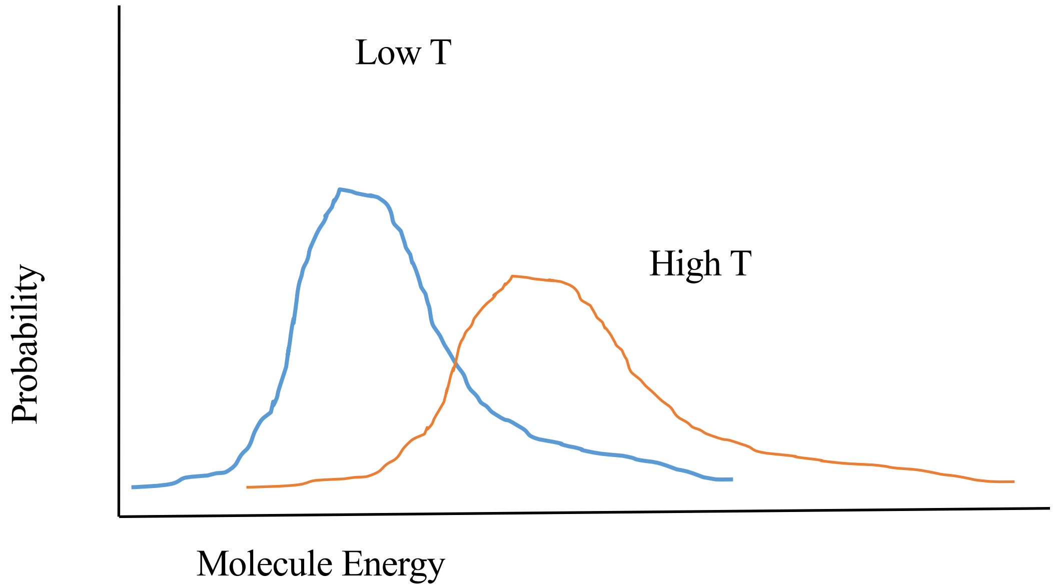
• Energy can be transmitted through a substance by molecular collisions (gas, liquid) and by vibrations (liquid(?), solid)

• Vibrations in a crystal are very effective at moving thermal energy.

Vapor Pressure

Temperature describes a mean energy stored in each degree of freedom

Some molecules are always in an energy state that favors a different phase



Why does H_2O change phase?

liquid-vapor	solid-liquid	solid-vapor

• Due to statistical fluctuations in energy among molecules, there are always some molecules crossing a natural interface.

• Under equilibrium conditions on boundaries of phase diagram, equal numbers go both ways. Two phases can coexist indefinitely (equilibrium).

• In interiors of phase-diagram regions, conditions favor more molecules going one way than the other. One phase will disappear over time (disequilibrium).

What determines equilibrium vapor pressure?

Number of molecules leaving solid or liquid must equal number of molecules leaving vapor phase.

Number leaving solid or liquid:

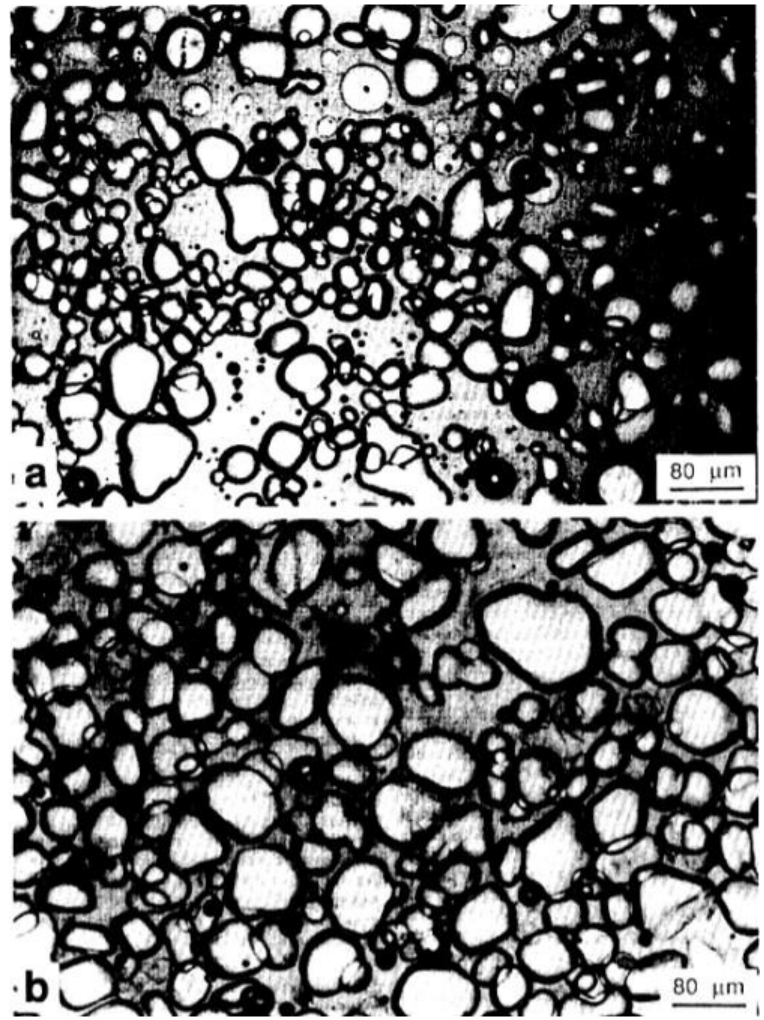
- increases with temperature T (more energy available to break H-bonds)
- is greater with fewer H-bonds to break to liberate a molecule (water *vs* ice)

Number leaving vapor phase:

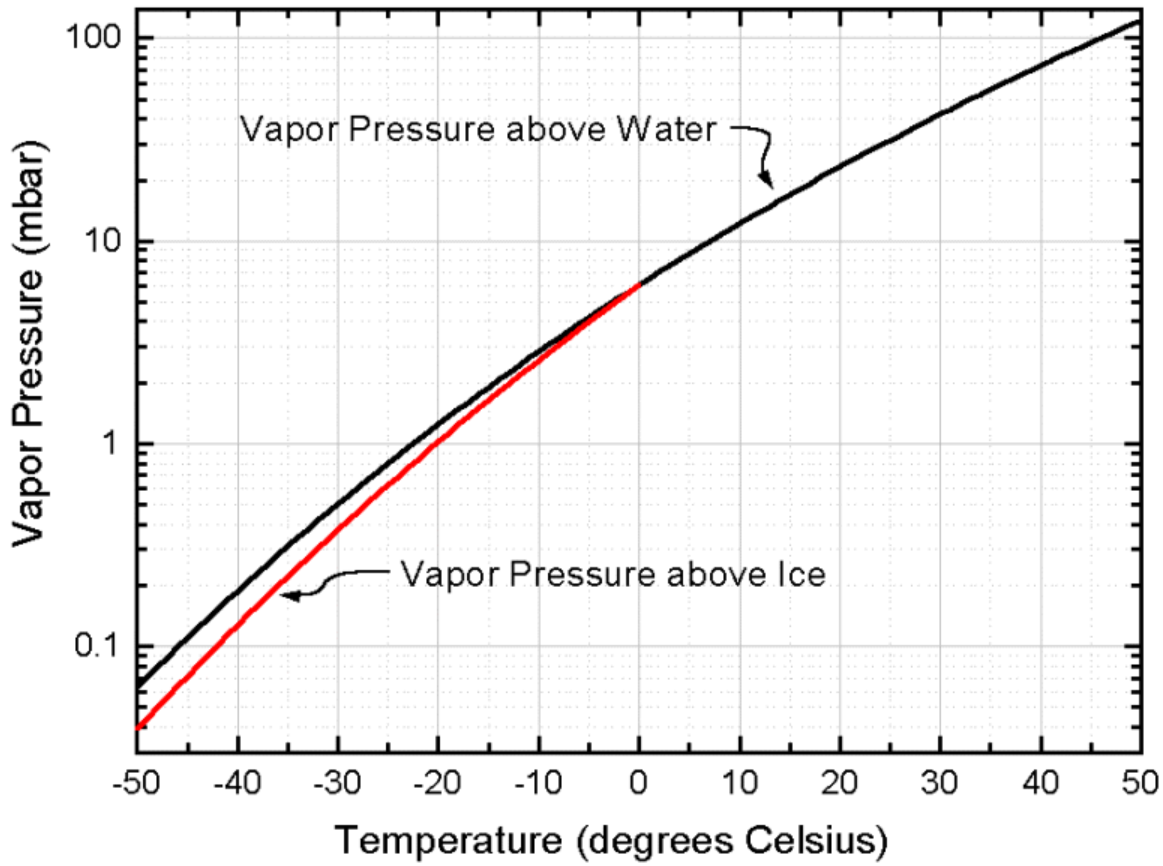
- is proportional to density of the vapor (molecules cm^{-3})
- increases as T decreases (slower-moving vapor molecules have less energy to get rid of to form H-bonds)

Metamorphism in snow pack

- Convex ice surfaces melt faster than flatter or more concave surfaces.
- Why do you think this is?
- What happens in snowpack at 0^{o}C?
- Large ice crystals grow at the expense of smaller ones.



Vapor Pressure over water and ice

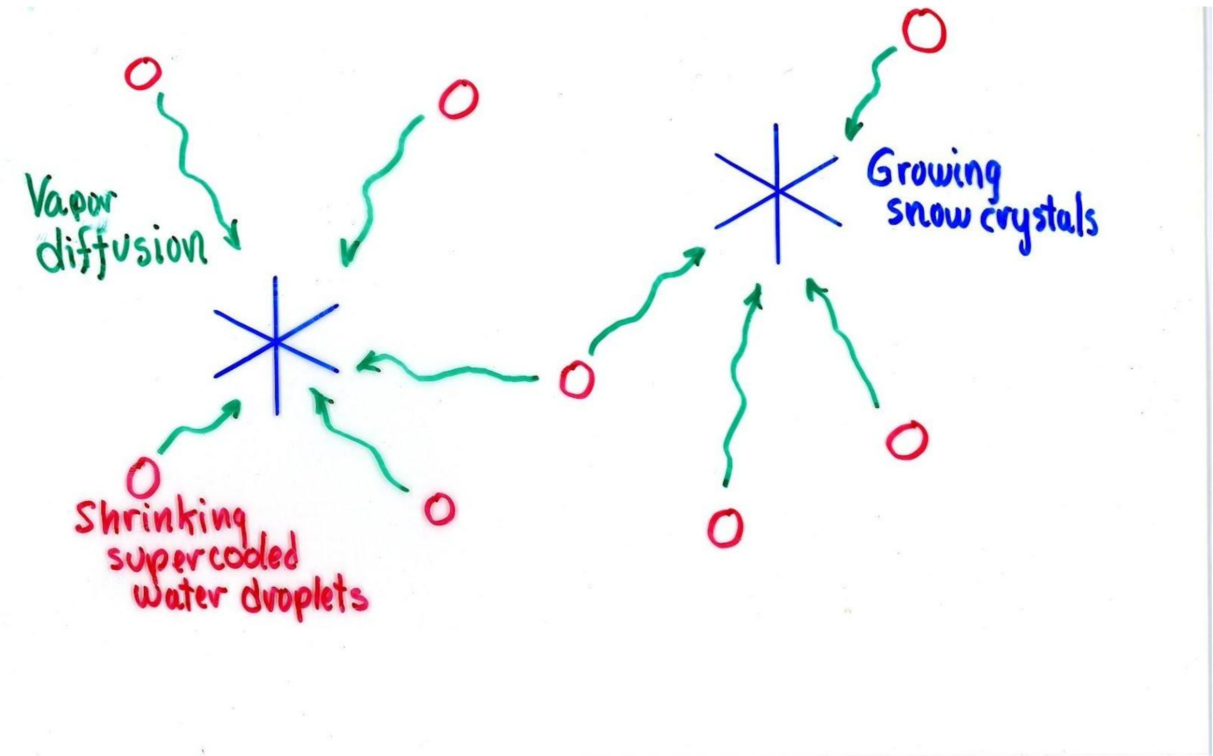


http://www.its.caltech.edu/~atomic/snowcrystals/ice/ice.htm

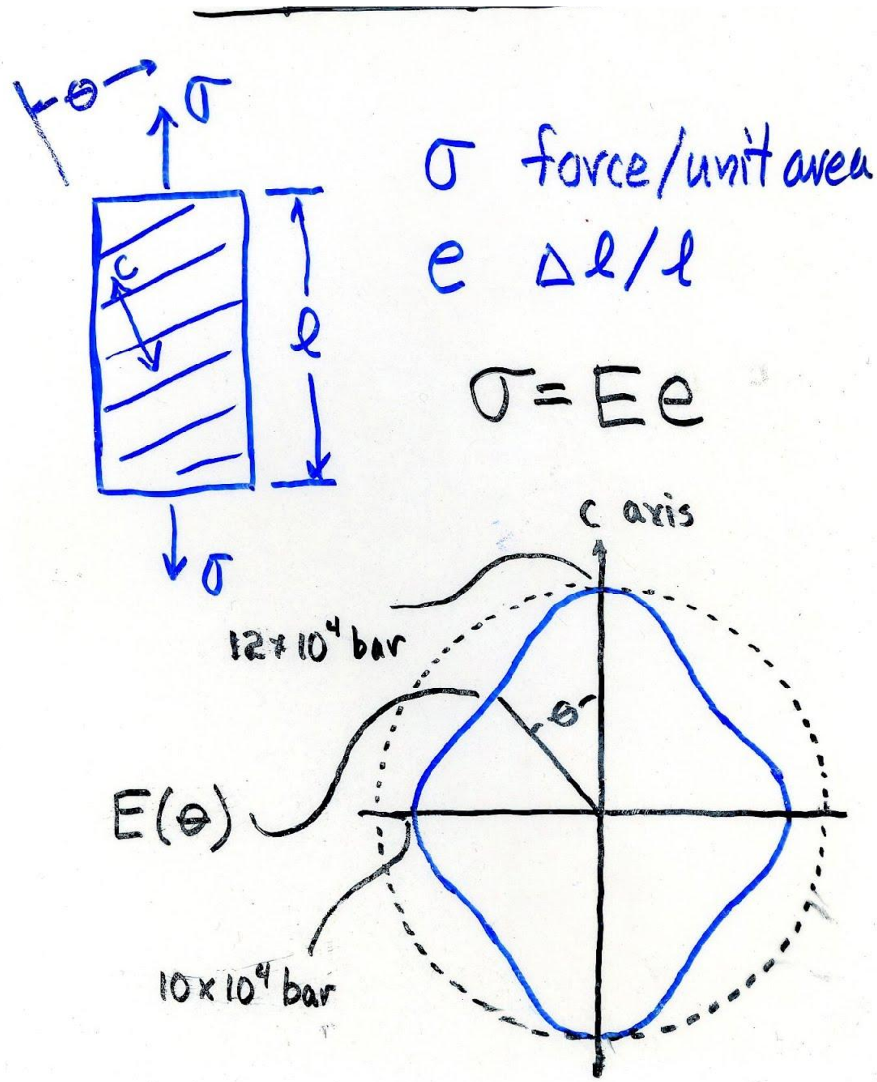
Supercooling

- Freezing Vs Melting point (Not always the same)
- Between -40 ^oC and 0 ^oC, ice crystals are energetically stable, but their formation needs a kick start Seed Crystal
- Water in Atmosphere can be pure enough to supercool -> freezing rain
- Glass vs. Supercooled liquid

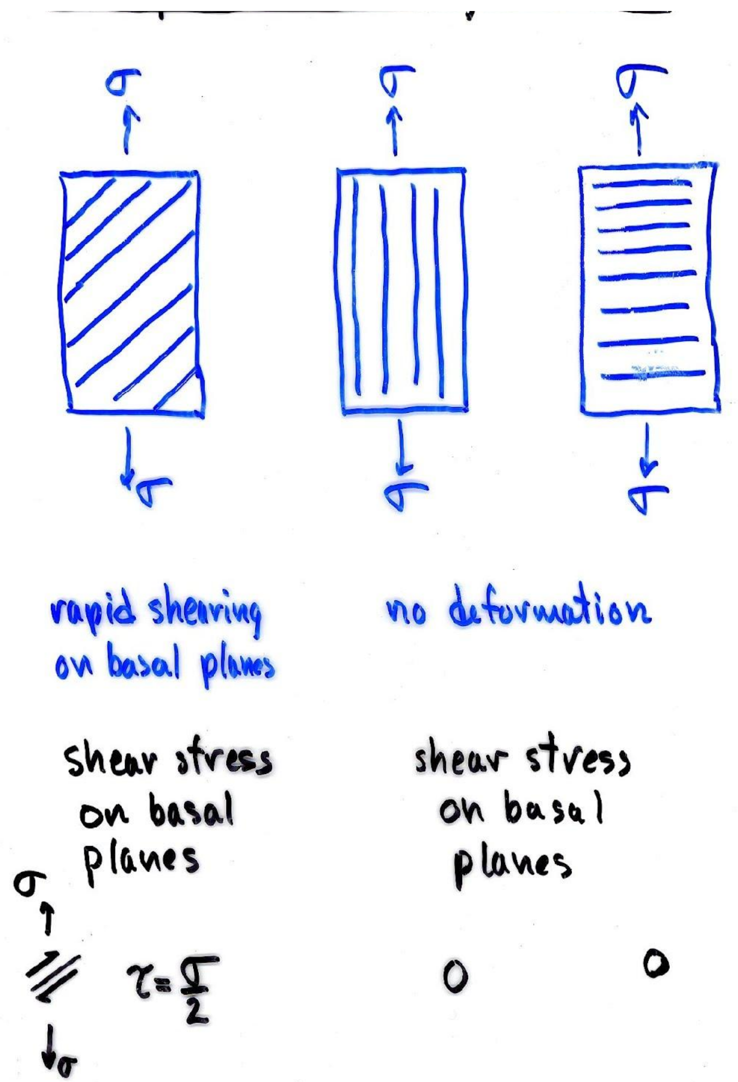
A Mode of Snow Crystal Growth in the Atmosphere



Elasticity of a Single Crystal



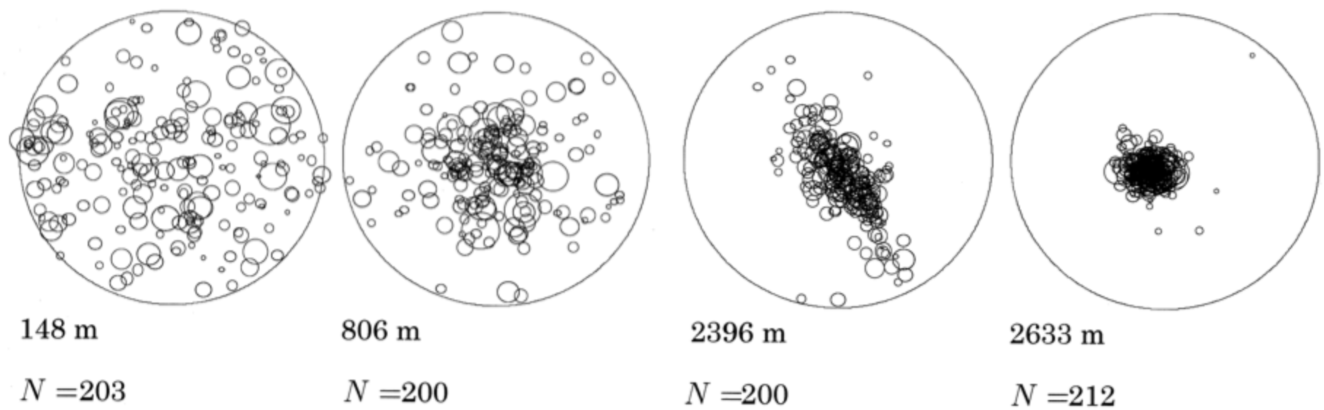
Creep of a Single Ice Crystal



Bulk Properties of Ice

- Natural ice (e.g. in glaciers or sea ice) is composed of many crystals (polycrystalline)
- Bulk properties may depend on the orientations of the crystals
- The statistics of the orientations of c-axes is called a c-axis fabric

Some Ice Fabrics



Schmidt plots

- Horizontal thin sections from NGRIP ice core, Greenland
- Circle location marks orientation of a c axis on a hemisphere
- Circle area indicates crystal size

Gagliardini et al. (2004) *J.Glaciol.*