

PHYSICAL CHEMISTRY

PHYSICAL PROPERTIES OF LIQUIDS

CHAPTER 1

State of a Substance

- The state of a substance depends on the balance between the kinetic energy of the individual particles (molecules or atoms) and the **intermolecular forces**.



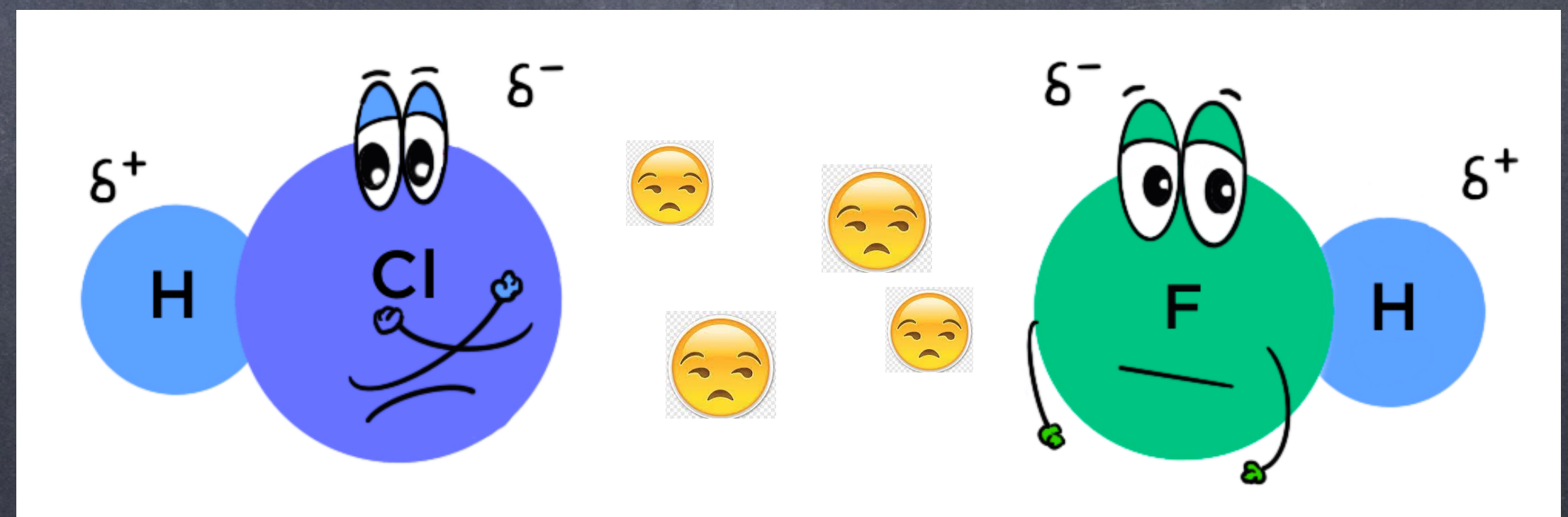
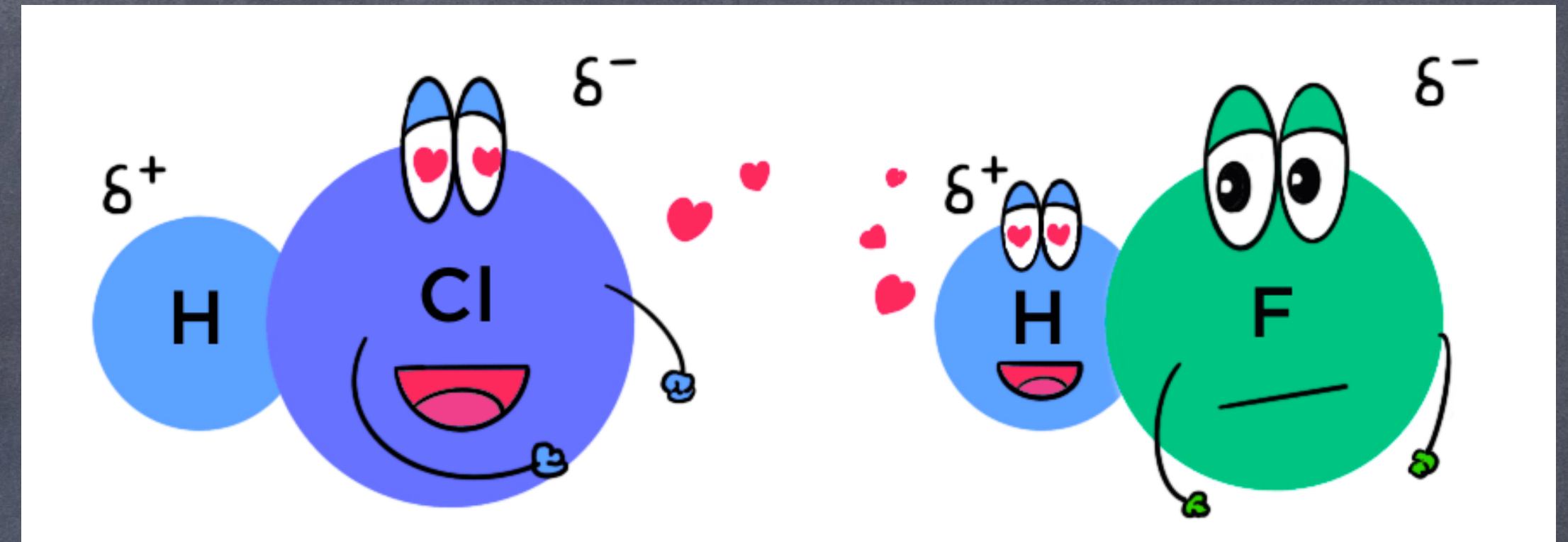
- The kinetic energy keeps the molecules apart and moving around, and is a function of the temperature of the substance and the **intermolecular forces** try to draw the particles together.

Intermolecular forces in liquids

- Molecules in liquids are held to other molecules by intermolecular interactions, which are **weaker** than the intramolecular interactions that hold molecules and polyatomic ions together.
- The three major types of intermolecular interactions are **dipole-dipole interactions**, **London dispersion forces** (these two are often referred to collectively as **van der Waals forces**), and **hydrogen bonds**.

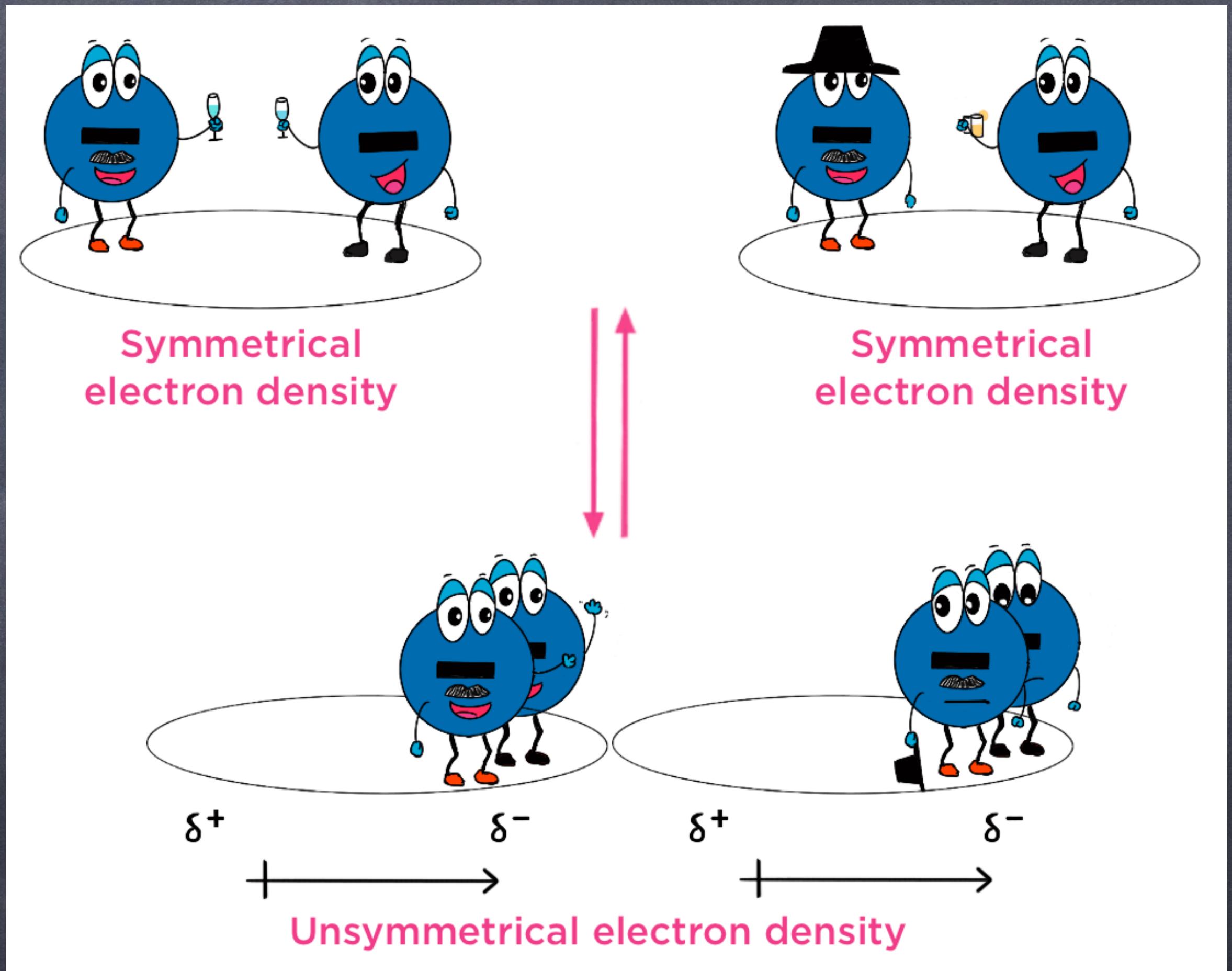
Dipole-dipole forces

- Dipole-dipole interactions exist between polar molecules.
- Effective only when polar molecules are very close together.
- Weaker than ion-dipole forces.



London dispersion forces

- Also known as instantaneous dipole-induced dipole intermolecular force.
- These types of forces exist between non polar molecules.
- Random motion of electrons can create an instantaneous dipole moment

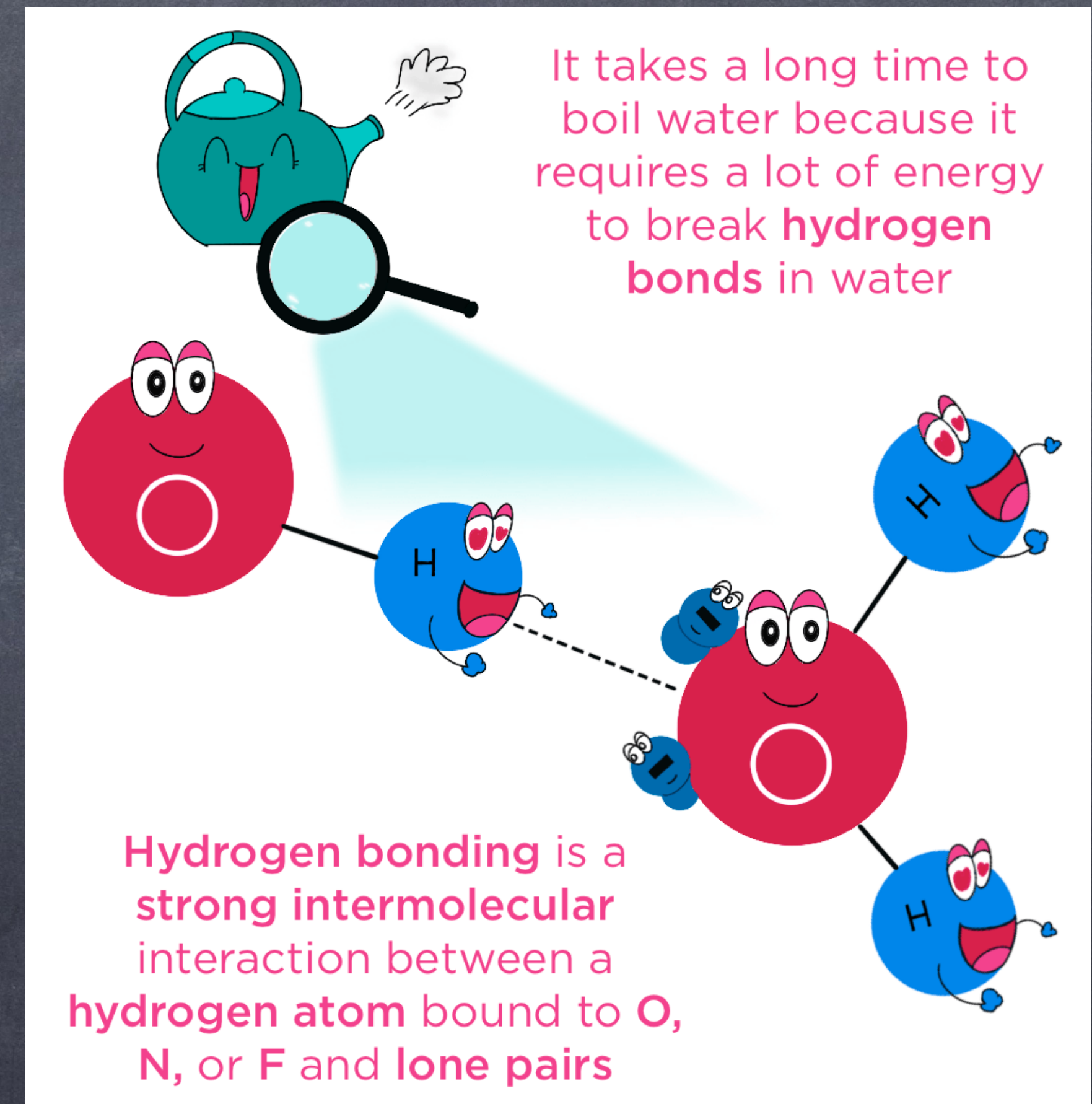


London dispersion forces in organic molecules

- The possibilities for these types of interactions go up with increasing **molecular size** and **surface**.
- The larger surface increases the chance for induced charge separation.
- The linear molecules have higher MP and BP because of increased interactions.
- e.g. n-Pentane(bp=36.4°C), Isopentane, Neopentane(bp=9.7°C)

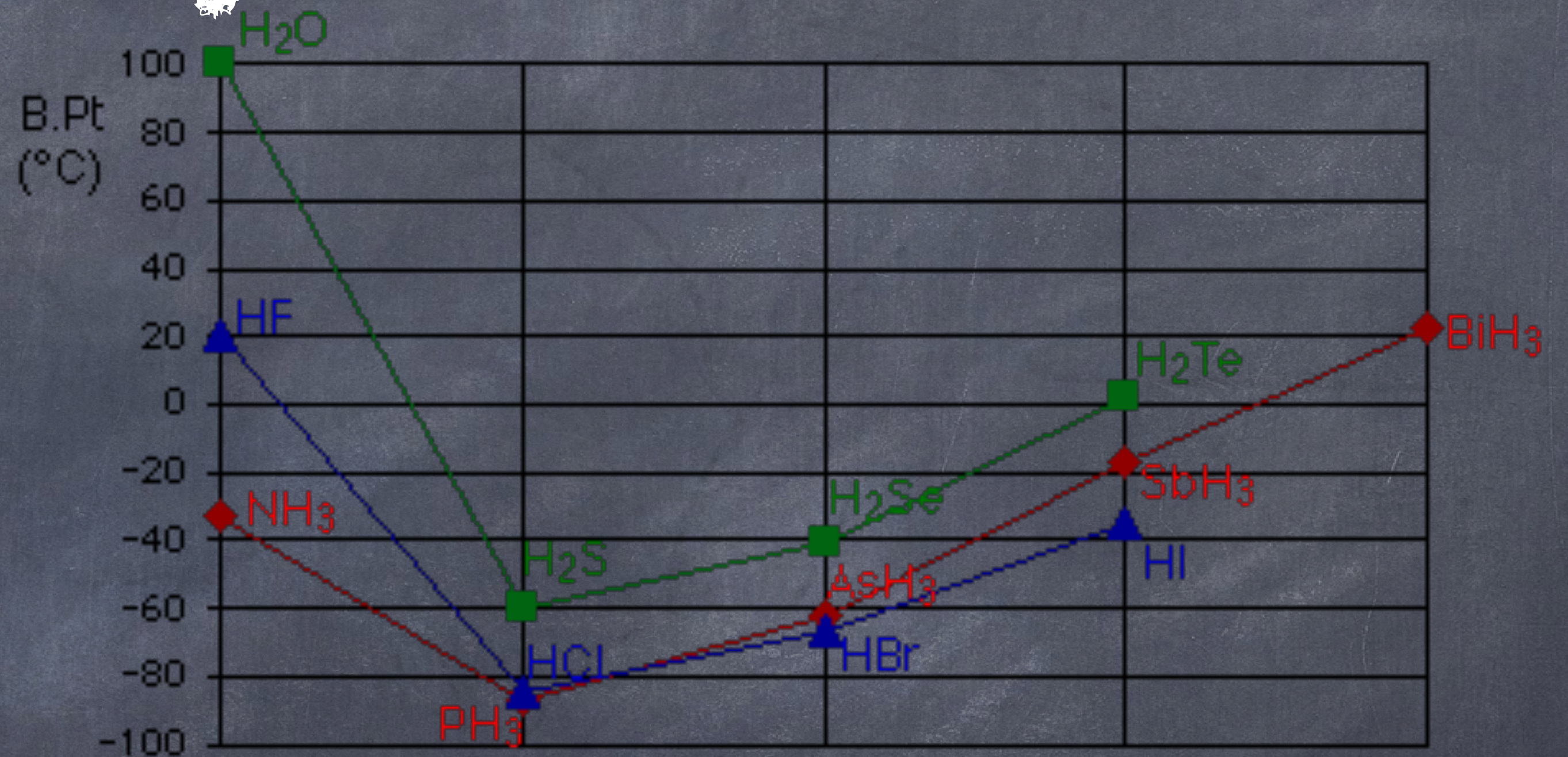
Hydrogen Bonding

A hydrogen bond is an intermolecular force (IMF) that forms a special type of dipole-dipole attraction when a hydrogen atom bonded to a **strongly electronegative atom (F, O or N)** exists in the vicinity of another electronegative atom with a lone pair of electrons.

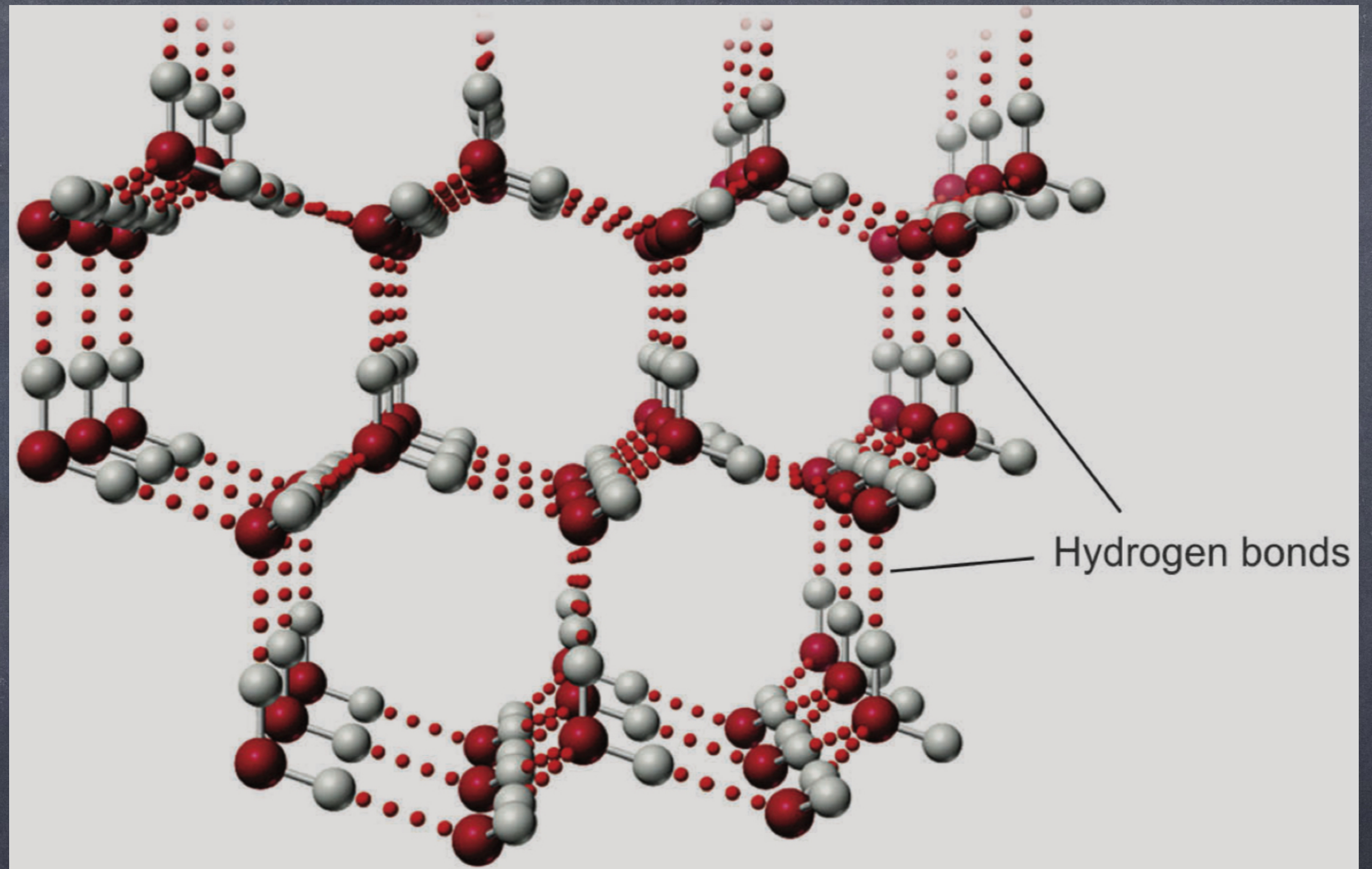


Significance of Hydrogen Bonding

- The high boiling point of water as compared to the expected value.
- The predicted value is very low.
- It could have gone as low as -60°C .



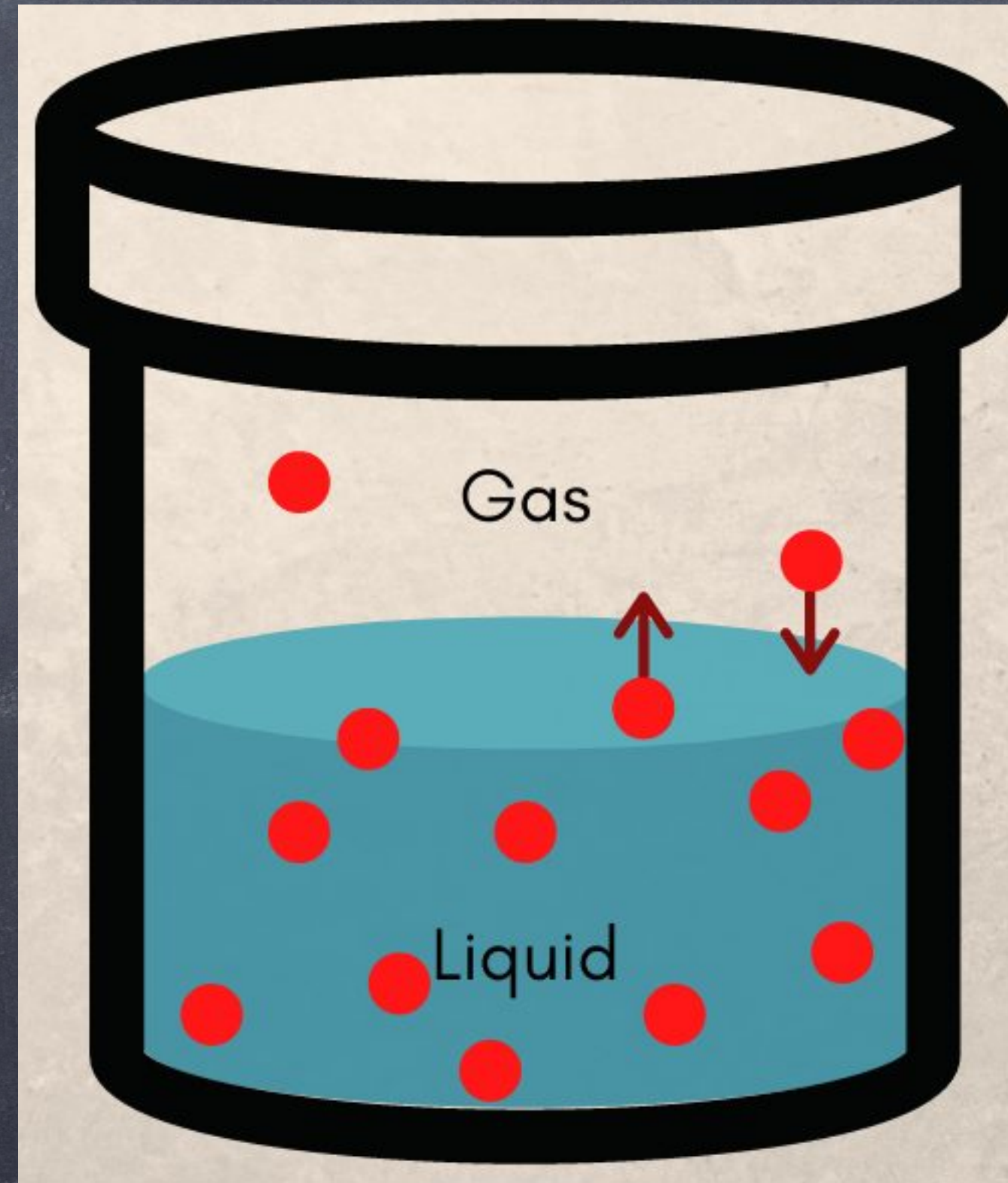
Hydrogen bonding is responsible for the expansion of water when it freezes.



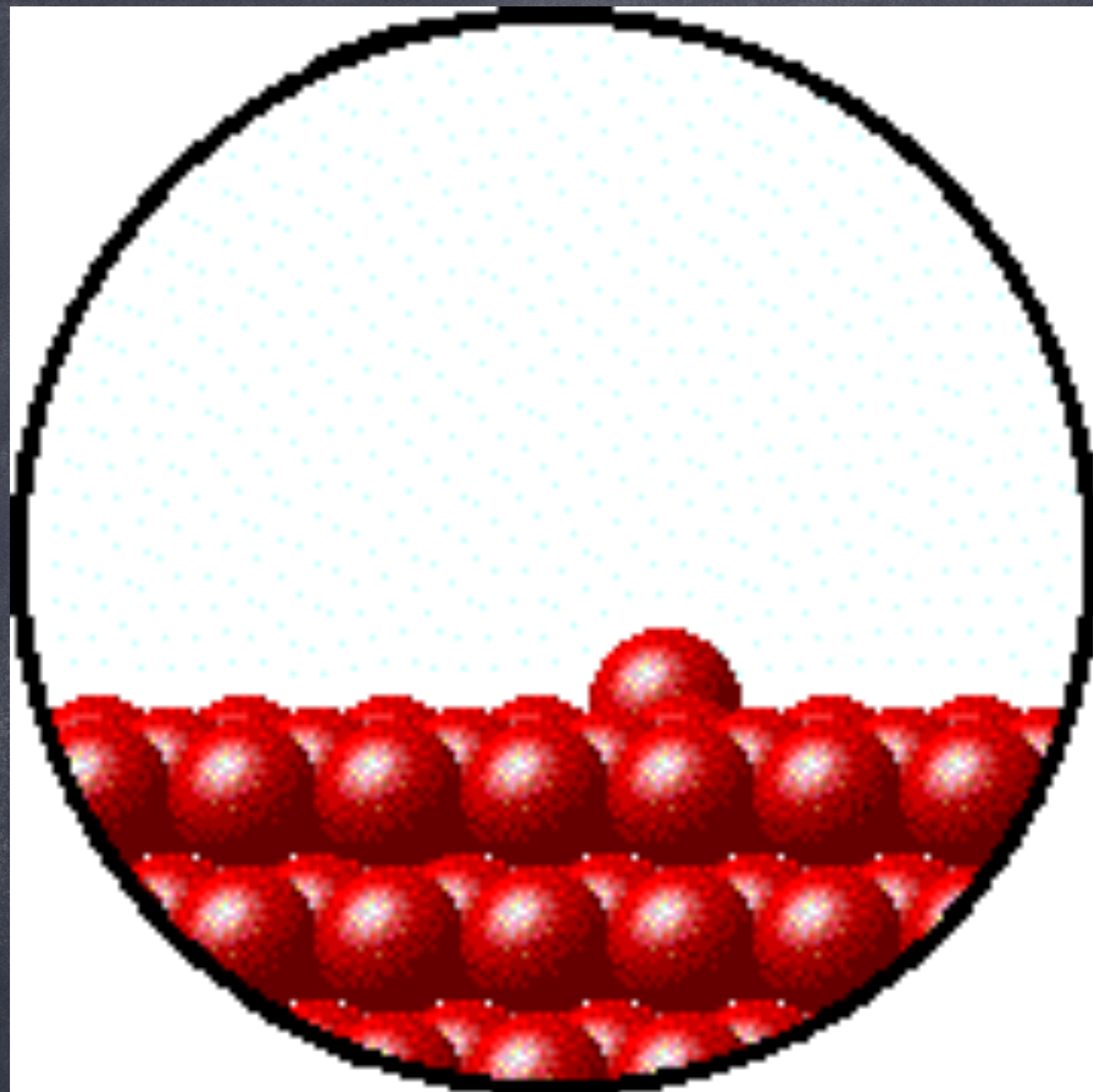
Vapour Pressure

Vapor pressure is the equilibrium pressure of a vapor above its liquid at a fixed temperature.

- At equilibrium, the evaporation rate equals the condensation rate.
- Molecules in vapour phase collide with the walls and lid of the container causing pressure.



- Evaporation and condensation occur at the liquid surface.
- Increasing temperature increases the rate of evaporation and increases vapor pressure.



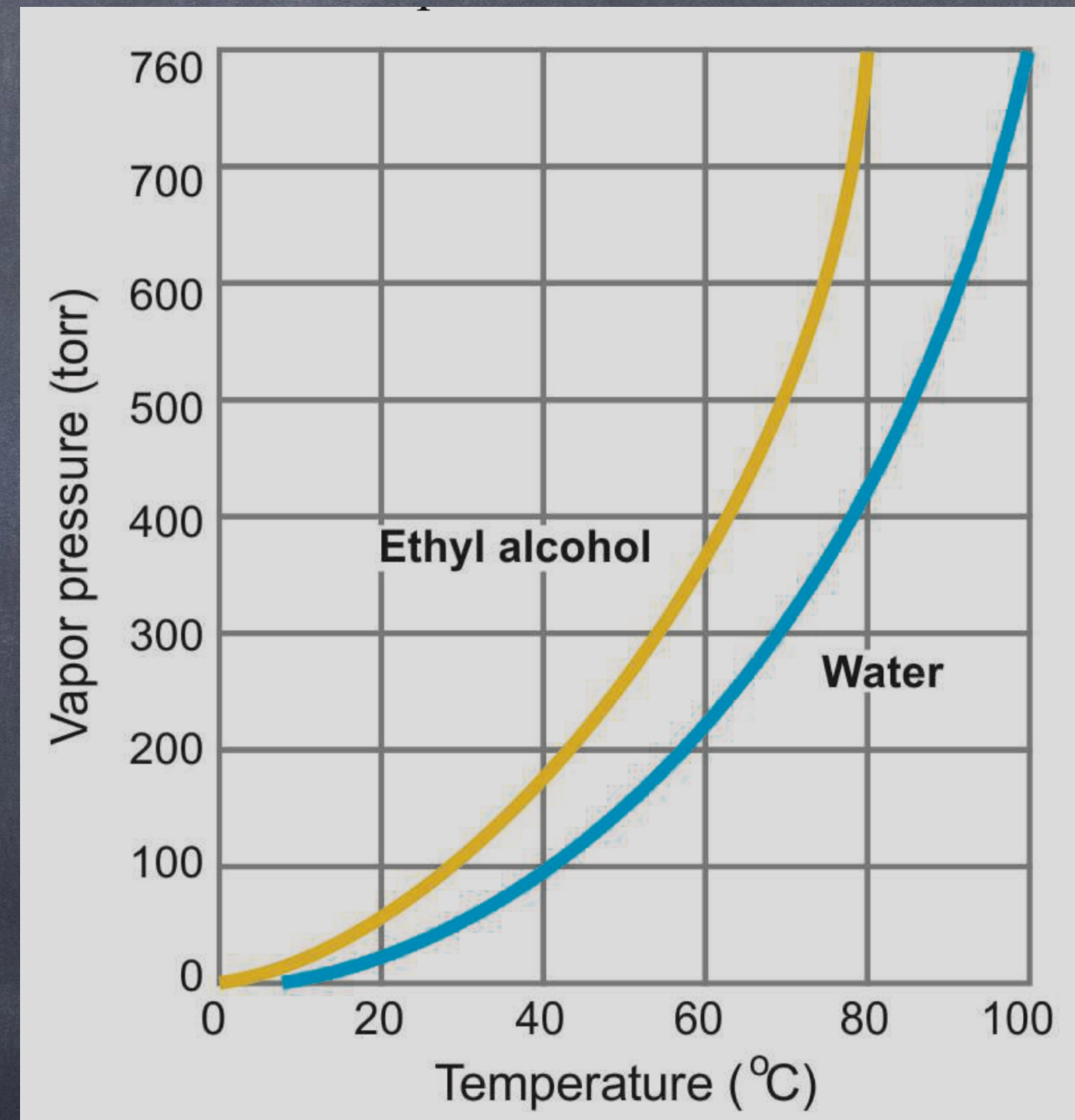
Microscopic equilibrium
between gas and Solid



Microscopic equilibrium
between gas and liquid

Effect of Temperature on Vapour Pressure

- At higher temperature, more molecules will have enough kinetic energy to escape from the liquid. At a lower temperature, fewer molecules have sufficient energy to escape from the liquid.
- The concentration of vapour molecules will be more at higher temperature.



What will be the effect of surface area on vapour pressure ?

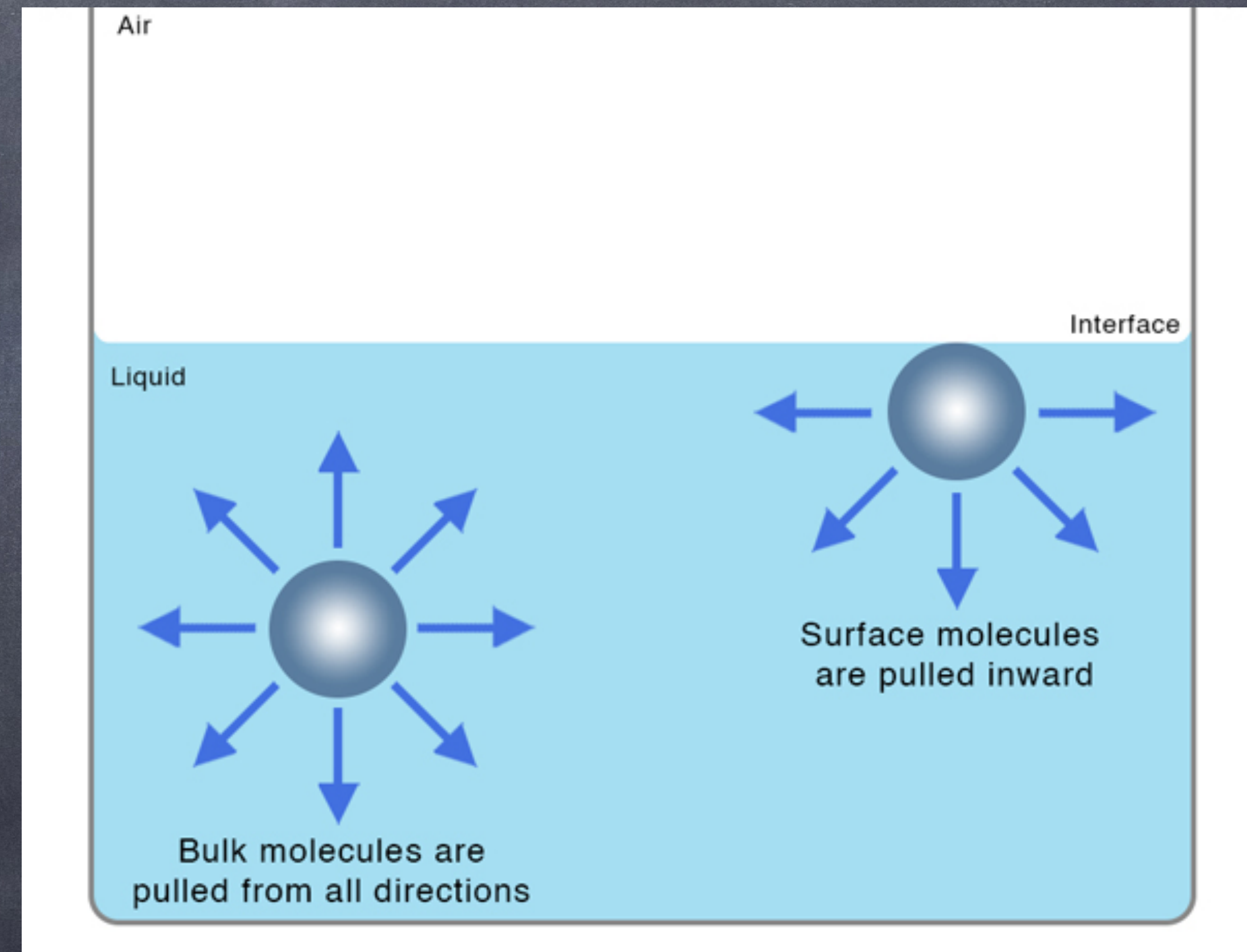
Boiling Point

- The boiling point of a liquid may be defined as the temperature at which the vapour pressure of the liquid is equal to the atmospheric pressure.

How does a pressure cooker
work?

Surface Tension

- The liquid surface is under tension due to imbalanced forces on surface molecules and it behaves like a stretched membrane.
- The liquid surface always tends to minimise the area in order to have minimum number of molecules at the surface.
- Surface tension decreases with increase in temperature.



Real life examples of surface tension



Surface tension helps dew drops stick to the grass and prevents them from spreading.



Surface tension prevents this flower from sinking.



Surface tension prevents a paper clip from sinking.



Surface tension helps insects to walk on water.

Viscosity

Viscosity is a measure of a fluid's resistance to flow.

- We can consider liquid to be consisting of molecular layers arranged one over the other.
- It is a measure of resistance to flow between adjacent layers of fluid.



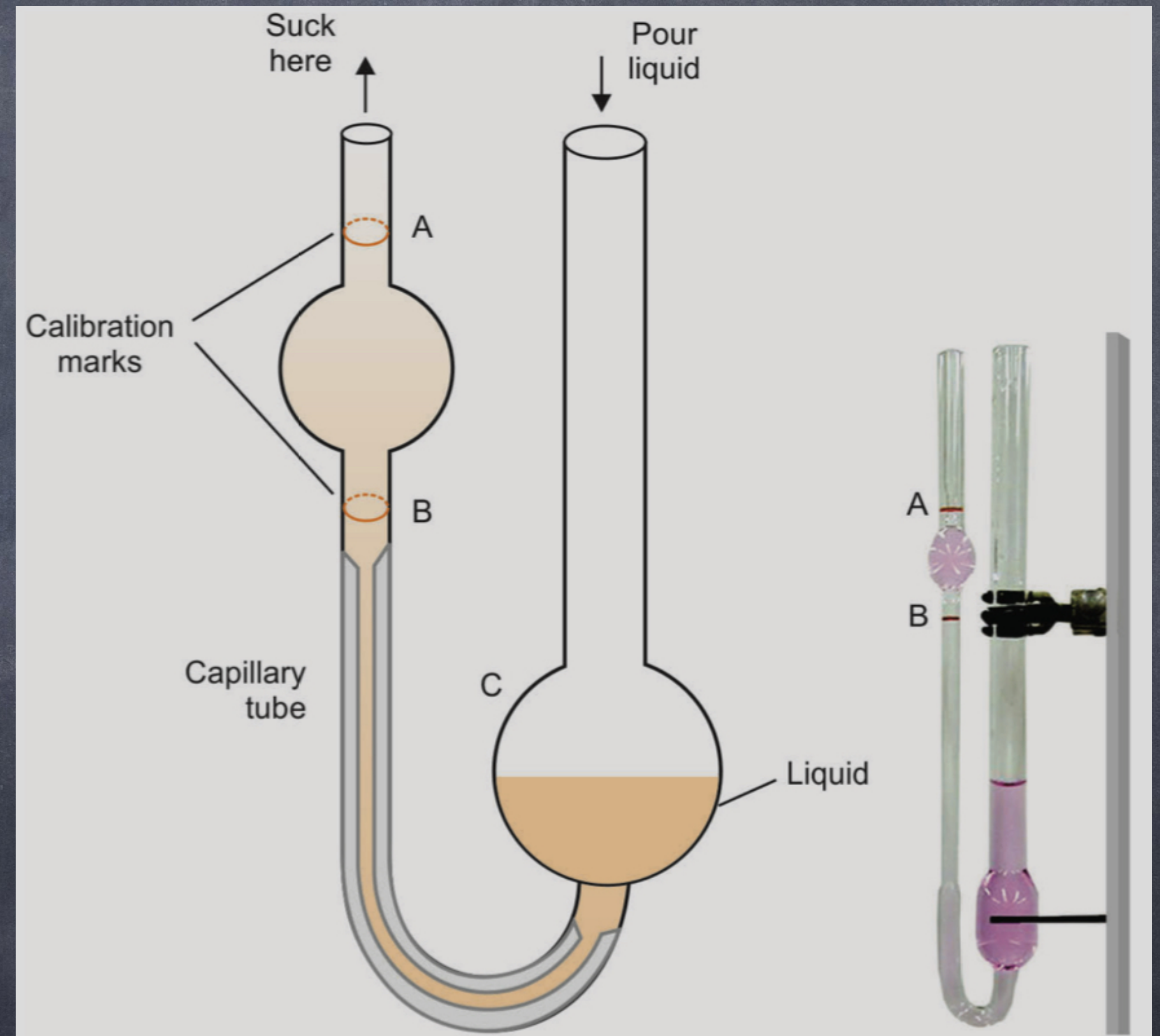
Water
Lower Viscosity
1.0 centipoise



Honey
Higher Viscosity
12,200.0 centipoise

Measurement of viscosity

- We can measure viscosity with the help of **Poiseuille's equation**.
- It is very difficult to measure the absolute viscosity using above equation.
- We can easily measure Relative Viscosity with respect to water using **Ostwald Viscometer**



Refraction

Bending of light when it travels from one medium to another is called refraction.



Light Refraction Through Glass and Water

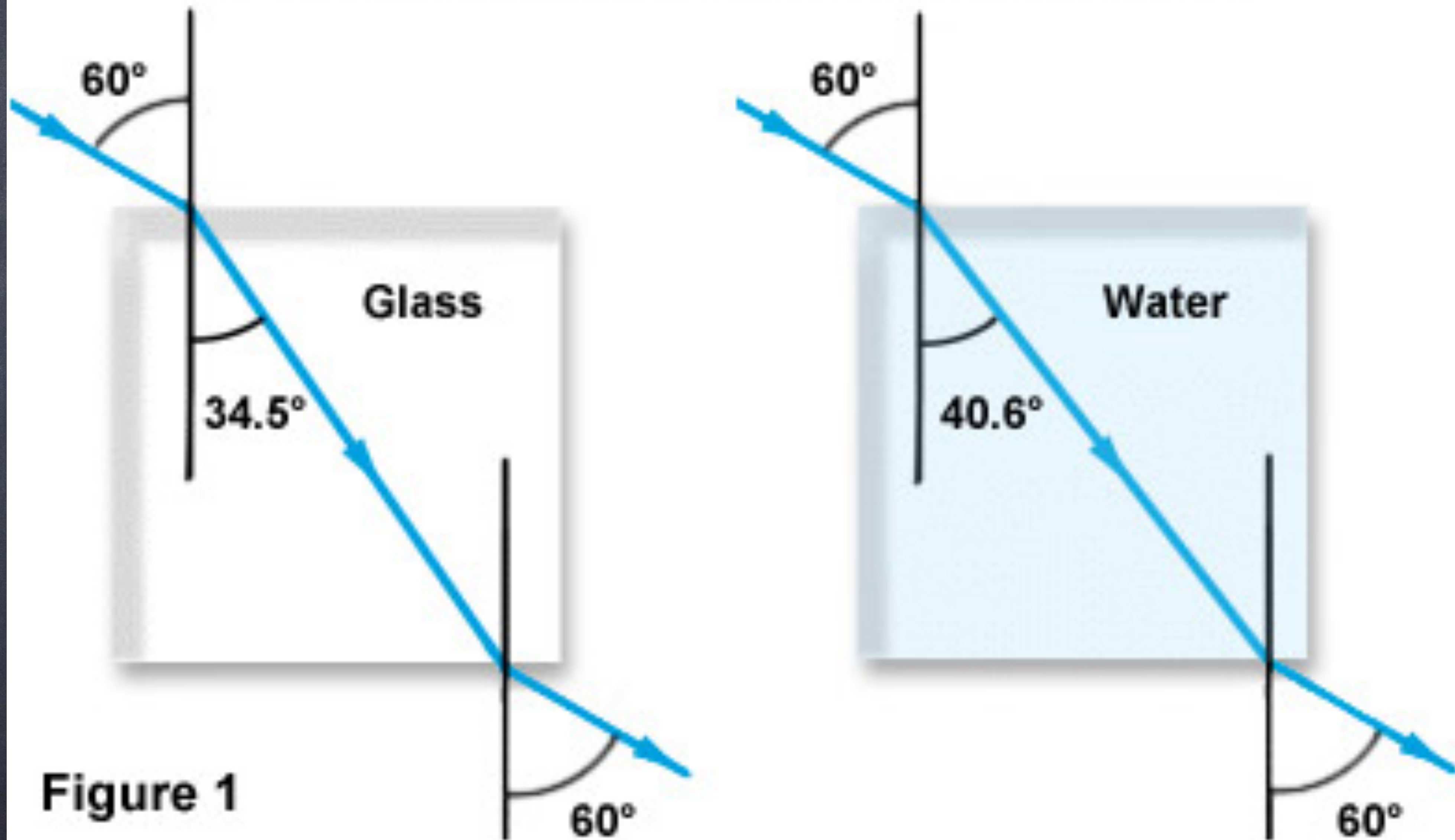


Figure 1

Refractive Index

- The refractive index (n) of a substance is defined as the ratio of the velocity of light in vacuum or air, to that in the substance:

$$n = \frac{\text{Velocity of light in air or vacuum}}{\text{Velocity of light in substance}}$$

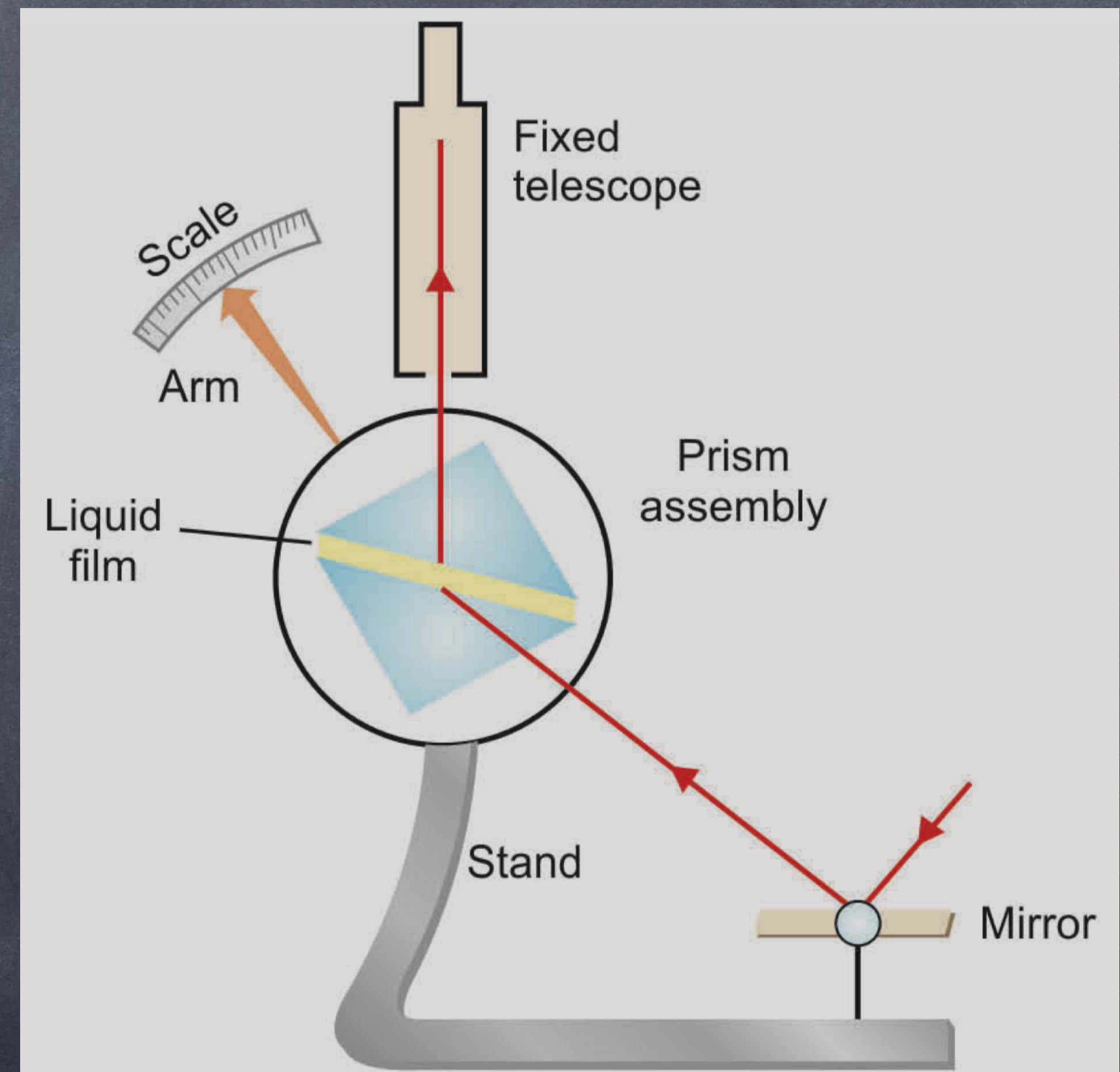
- The refractive index of the liquid with respect to air is given by Snelle's Law:

$$n = \frac{\sin i}{\sin r}$$

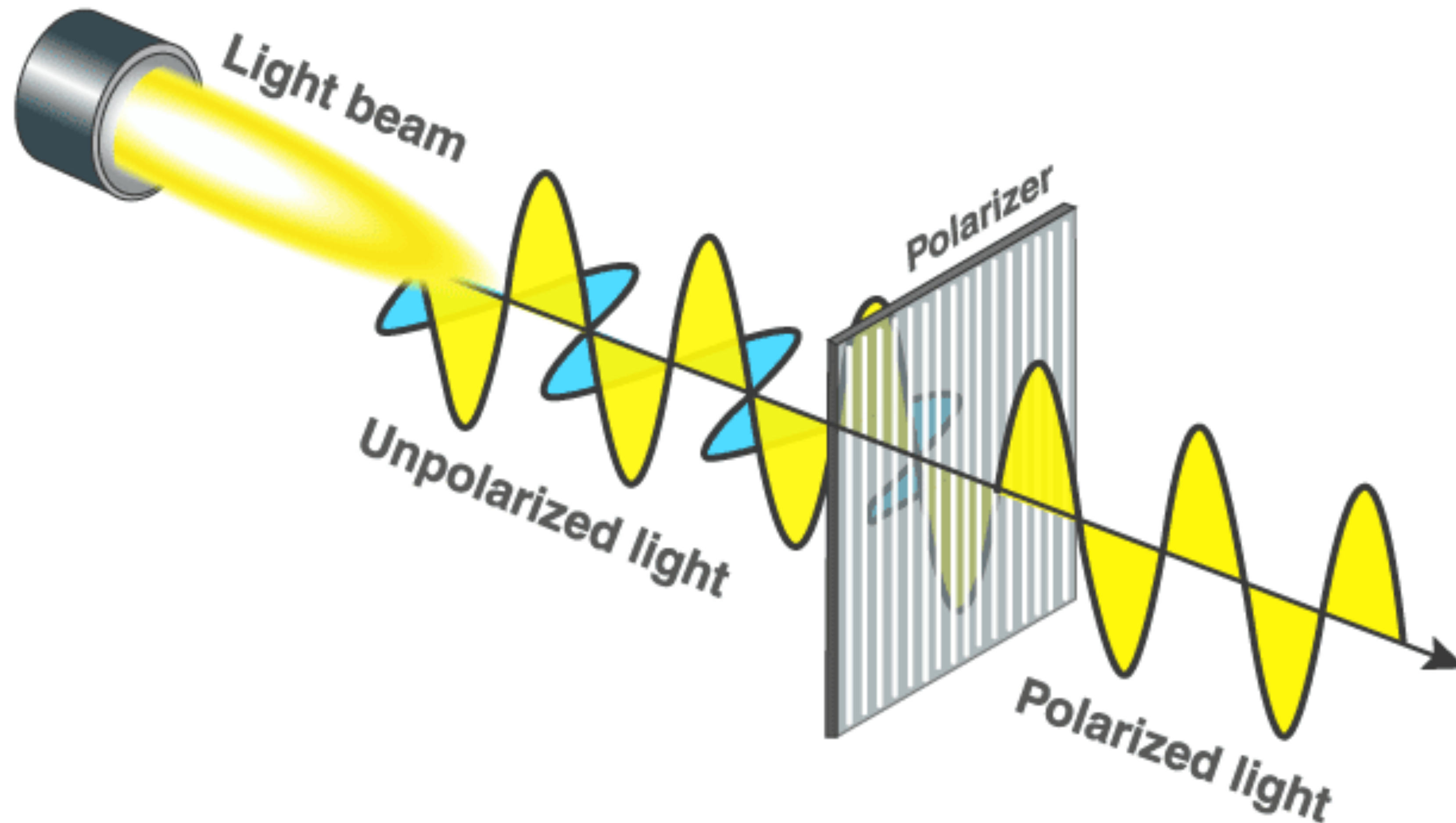
- The refractive index of a liquid can be easily determined to a high degree of accuracy. It is a characteristic property of a liquid.
- Refractive index varies with temperature and wavelength of light used.

Determination of Refractive Index

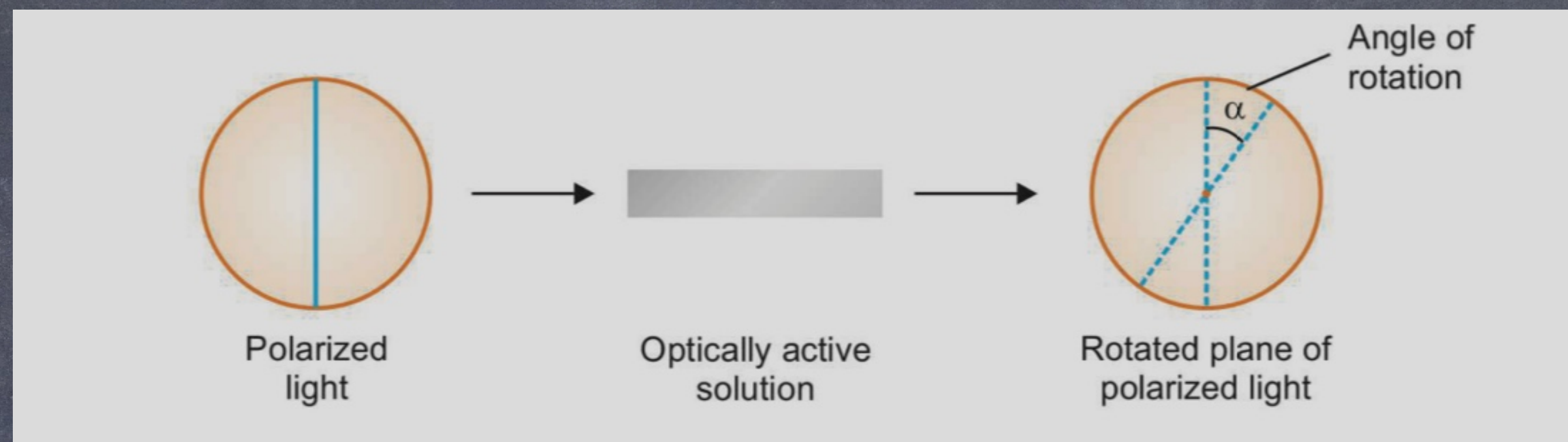
The refractive index of a liquid can be determined with the help of an instrument called **Abbe Refractometer**.



Polarization

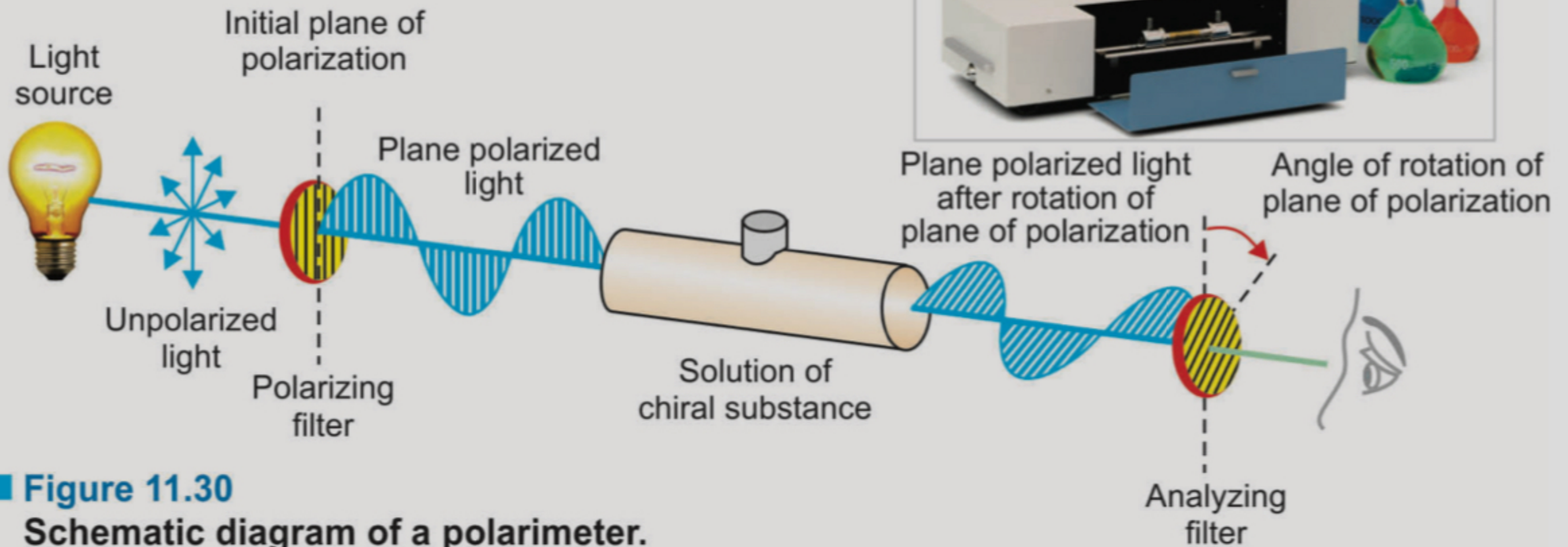


Optical activity



- When a plane polarized light passes through certain organic compounds, the plane of polarized light is rotated.
- A compound that can rotate the plane of polarized light is called **optically active**.
- The property of a compound is called **optical activity**.

Measurement of optical activity



■ **Figure 11.30**
Schematic diagram of a polarimeter.