Lecture 22

Vapor pressure

Vapor pressure of a liquid is a pressure of a vapor over a liquid when liquid and vapor are in dynamic equilibrium. A liquid in a sealed beaker is actually a dynamic system. Some molecules of liquid are evaporating to form vapors while some molecules of vapor are condensing to form liquid. At equilibrium the rate of evaporation and condensation are equal and system become stationary. The vapors exert pressure on the liquid this pressure is called vapor pressure. Vapor pressure of a liquid depends upon Nature of a liquid and Temperature of a liquid

Nature of a liquid:

The liquids which have weak intermolecular forces are volatile and its molecules can escape easily from surface of the liquid hence its vapor pressure is high while the liquids with strong intermolecular forces have low vapor pressure.

Temperature of a liquid:

Vapor pressure increases with increase in temperature this is because the rate of evaporation also increases with increase in temperature.

Heat of vaporization:

It is the amount of heat which is required to vaporize one mole of a liquid into at a pressure of one atmosphere. It is denoted by ΔH_{vap}. The vapor molecules condense to form a liquid and eventually a stage come when the rate of evaporation becomes equal to rate of condensation.

Dynamic equilibrium of vapor pressure:

The vapor molecules condense to form a liquid and eventually a stage come when the rate of evaporation becomes equal to rate of condensation. A liquid is in dynamic equilibrium with its vapor phase, the rates of evaporation and condensation are When exactly equal to each other. If you imagine putting a pure liquid into a closed container, the vapor pressure is initially close to zero, and as a result, the rate of condensation is also close to zero. The rate of evaporation liquid.is not zero, so the vapor pressure builds up to the point where the rates of evaporation and condensation are equal to each other. At this point, the system is in dynamic equilibrium, and the partial pressure of vapor in the container is equal to the equilibrium vapor pressure of the liquid. At this point molecules are constantly entering and escaping from the liquid.

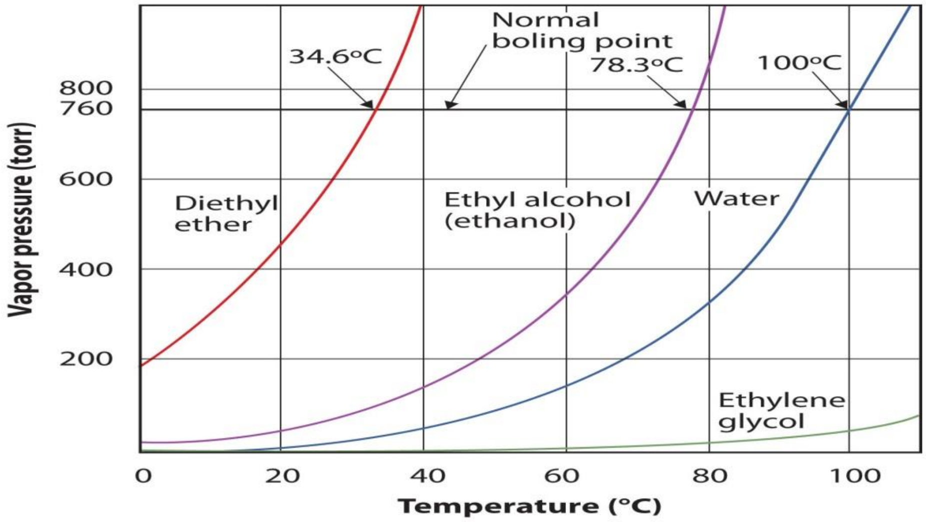
Vapour pressure and Kinetic energy:

As temperature of a liquid raised the kinetic energy of molecules increases and they collide with each other eventually the rate of collision become so high that the particles break all intermolecular forces and move independently due to which change in physical state occurs.

Vapor pressure and Temperature:

Vapor pressure increases with increase in temperature. The molecules in liquid become more energetic at high temperature and more molecules can escape from liquid into gas phase.

Each time as we raise the temperature the vapor pressure not only goes up but it goes up much more each time we raise the temperature with same amount. It means that if we plot the graph between vapor pressure and temperature it shows a curved line instead of straight. The curve resulting from such a plot for water, ethanol and diethyl ether is as fellow.



We can get the linear relation between vapour pressure and temperature by using the following equation.

$$\ln(Pvap) = -\Delta Hvap/R\ (1/T) + C$$

Where $\Delta Hvap$ is enthalpy of vaporization, R is universal gas constant and C is a constant for each liquid. We can find enthalpy of vaporization by measuring Pvap at several temperatures. We can combine the equation as because to solve Pvap at different temperatures as C does not depend on temperature so it is exempted.

$$\ln(PvapT1) - \ln(PvapT2) = \Delta Hvap/R\ (1/T2 - 1/T1)$$

$$\ln(PT1/PT2) = \Delta Hvap/R\ (1/T2 - 1/T1)$$

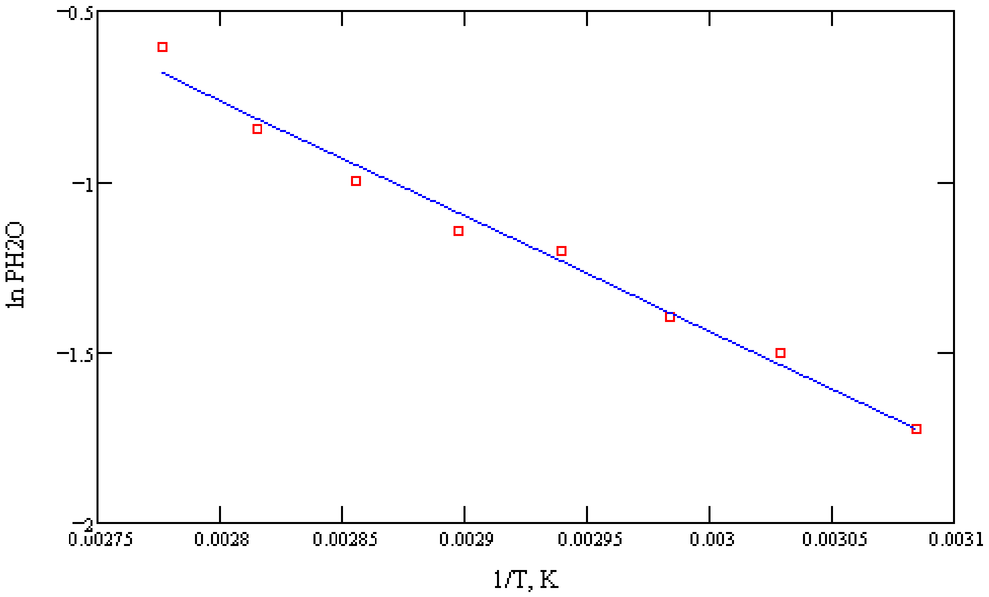
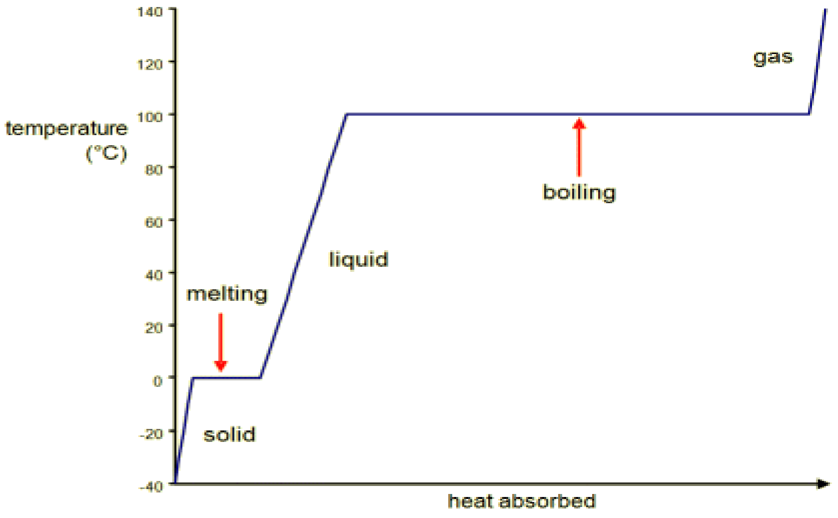


Fig 2 Linearized P-T plot

Changes of State:

When solid is heated it is converted into liquid and when liquid is heated will boil and converted into gaseous state. Energy is required for melting of solid into liquid. For example when ice is heated random vibration of water molecule increases, lattice is broken down and it changes into liquid. Energy is needed to break the hydrogen bonds between the molecules. When temperature of ice reaches at 0°C it remains constant until all solid changes into liquid after that the temperature will increase again. When temperature of liquid water reaches at 100°C it remains constant until all liquid is converted into gas. Following graph shows the melting and boiling of water



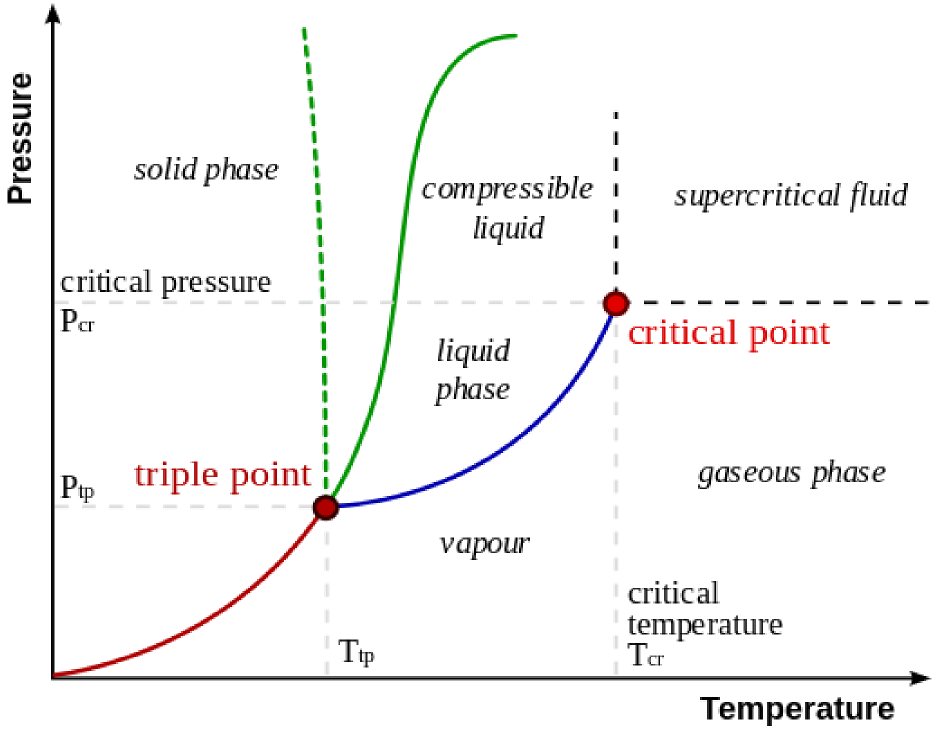
Melting Point:

The temperature at which vapor pressure of solid and liquid become identical is called melting point. The temperature at which the solid and liquid has same vapor pressure while the total pressure at that time is one atmosphere is called normal vapor pressure. Boiling occurs when vapour pressure of liquid is equal to the environmental pressure.

Phase Diagrams:

Phase diagrams shows that which states of a substance can exist at given temperature and pressure. These diagrams represent the conditions of close system. There are three major points in phase diagram

1. Triple point
2. Critical point
3. Phase equilibrium lines



Experiment 1:

At 1atm when the initial temperature of ice is -20°C it is heated till 0°C no change in state occurs and no vapours are formed because vapour pressure of substance is not 1atm at that temperature at 0°C ice starts melting but still no vapours are formed. At 100°C when the pressure of water is 1 atm it starts melting.

Experiment 2:

When the pressure is kept 2torr at -20^{o}C and temperature is increased at -10^{o}C ice evaporates into vapours directly without melting into liquid state. The process in which liquid directly evaporates into gaseous state without passing from liquid state is called sublimation.

Experiment 3:

At the pressure of 4.588torr while the temperature of ice is -20^{o}C it is started heating no change in phase occur until temperature reaches at .0098^{o}C

Triple Point:

The temperature and pressure at which three different phases, such as gaseous, liquid, and solid phases, of a particular substance can coexist in equilibrium. Liquid changes to vapor as temp increases, but goes through intermediate "fluid" region which is neither true vapor nor liquid.

Critical Temperature:

Temperature above which vapor cannot be liquefied no matter what pressure is applied is called triple temperature.

Critical Pressure:

The pressure which is required for liquefaction at critical temperature is called critical pressure. Melting point of water decreases as external pressure increases contrary to other substances as ice is less dense than water.

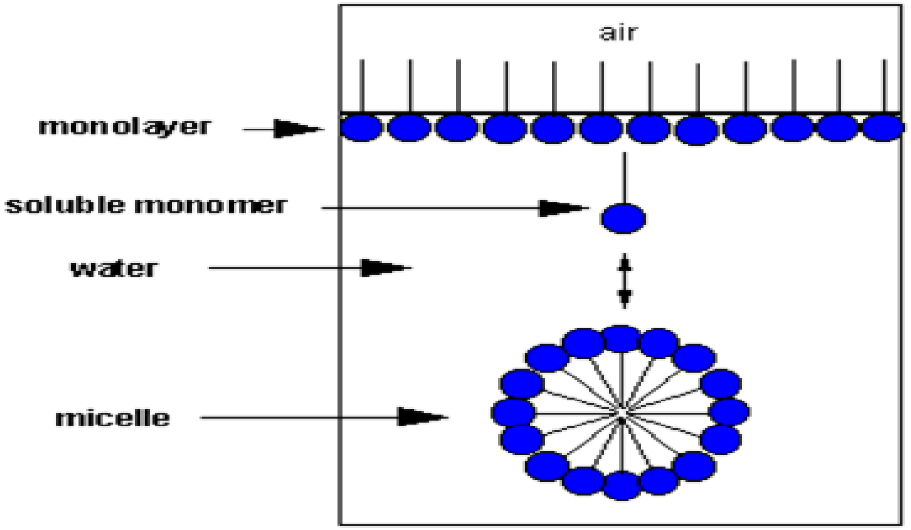
Lecture 23-24

Surface Tension

The force that causes the molecules on the surface of a liquid to be pushed together and form a layer. The surface of any liquid behaves as it is covered by a stretched membrane. Small insects can walk on water without getting wet. The membrane is obviously quite strong: it will support dense objects, provided they are small and of the right shape - a needle, a small square of aluminium sheet, a razor blade, and small insects.

Micellar Solublization:

Surfactants are compounds that lower the surface tension between two liquids or between a liquid and solid. Surfactant molecules accumulate between interfaces (surface forming a boundary between two immiscible liquids) of water soluble and water insoluble compound. The hydrocarbon chain of surfactant penetrates into the outer most layer of water insoluble compound. Micelles (aggregate of surfactant molecules) form around the water insoluble compounds and bring them into solution in an aqueous medium. This phenomenon is called miceller solublization. The inverted micelles formed by oil-soluble surfactant which dissolves in a hydrocarbon solvent and may push water-soluble compound located in the center of the micelle, out of contact with the solvent.



Micelles of Non Ionic Surfactants:

Micelles of nonionic surfactants consist of two parts an outer shell and inner core. Outer shell is polyethylene glycol moieties mixed with water and inner core is formed by the hydrocarbon moieties. Some complex like benzoic acid and phenols form complex with polyethylene glycol by hydrogen bonding. These compounds are more soluble in liquids of intermediate polarity such as ethanol and ethyl ether. These compounds are found in outer aqueous polyethylene glycol the outer shell of nonionic micelles on sollublization. Drugs which are oil soluble and lipid soluble can be solubilized by micellar solublization.

Solubility trend:

Micellar solublization depends on the existence of micelles. A critical micelles concentration (CMC) is necessary to start dissolution. Above CMC the amount solubilized is directly proportional to the amount of surfactant because above CMC all the surfactant added in solution is present in micellar form and as number of micelles increases extant of solublization increases. The compounds which are extensively soluble increase the size of micelles in two ways by increasing the size of by swelling because their core volume increases or the number of surfactant molecule increases per micelle.

Foams:

Foams are formed by the dispersion of gas in liquid or solid. Liquid foams are formed by soaps and detergents. Examples of solid foam are sponges.

Foaming Agents:

The chemical additives which promote the formation of foams and stabilize them are called foaming agents. These are useful in pharmacy in the composition of toothpaste.

Anti-foaming agents:

Antifoaming agents are chemical additive that reduces and hinder the formation in industrial processes. In pharmaceutical industry it is useful in aerobic fermentation and steam boilers.

Detergent:

Detergent is surfactant or mixture of surfactant used for removal of dirt, grease and grime. In the process of detergency first of all the dirt to be cleaned is wetted. Then defloculation occurs in which dirt particals are separated from the surface. After defloculation a suspension of surfactant and dust particles is formed. The dirt particles emulsify or solubilize within the detergent and finally these are washed away with water.

Structural Classification of Surfactants:

A single surfactant can possess one or more hydrophobic or hydrophilic ends. On the bases of presence of ions surfactants are classified into four types:

1. **Anionic Surfactant:**

   When hydrophilic part of surfactant consists of negatively charged ions like sulphonate or sulphate ion this surfactant is called anionic surfactant. Basic soaps are anionic surfactants. They are the metal salts of long chain fatty acids as lauric acid. Sodium dodecyl sulfate or Sodium Lauryl Sulfate is used in toothpaste and ointments. Triethanolamine dodecyl sulfate is used in shampoos and other cosmetic preparations.Sodium dodecyl benzene sulfonate is a detergent and has germicidal properties. Sodium dialkvlsulfosuccinates are good wetting agents.

2. **Cationic surfactants:**

   When hydrophilic part of surfactant consists of positively charged ion like ammonium ion is called cationic surfactant. These are chiefly quaternary ammonium compounds. They have bacteriostatic activity probably because they combine with the carboxyl groups in the cell walls and of microorganisms by cation exchange, causing lysis. Among the most popular antiseptics in this category are benzalkonium chloride, cetylpyridinium chloride and cetyltrimethylammonium bromide etc.

3. **Ampholytic surfactants:**
   These are consisting of both negative and positive hydrophilic ends e.g. dodecyl-B-alanine. These are usually used in shampoos, fungicides etc.

4. **Nonionic surfactants:**
   Nonionic surfactant is the nonelectrolyte type. Generally, hydrophilic group is polyoxyethylene group. Nonionic surfactant is used as detergents for kitchen and clothes, emulsifiers for cosmetics and food additives. Widely used in pharmaceutical formulations e.g. Tweens, Spans, Brij and Myrj. They are polyethylene oxide products.
   Surfactants based on sorbitan are of pharmaceutical importance. Esterification of the primary hydroxyl group with lauric, palmitic, stearic or oleic acid forms sorbitan monolaurate, monopalmitate, monostearate or monooleate. These are water insoluble surfactants called Span 20, 40, 60 or 80, respectively. Addition of about 20 ethylene oxide molecules produces the water-soluble surfactants called polysorbate or Tween 20, 40.,60 or 80.

Shapes of surfactants in Colloidal Solution:

The main shapes of surfactants in colloidal solution are cone shape surfactant that results in normal micelles, champagne cone shape surfactant resulting in reverse micelles with control of their size with water content e.g. interconnected cylinders Planar lamellar phase Onion-like lamellar phase.

Shapes of Micelles:

Normal spherical micelles:

In dilute aqueous solutions micelles are approximately spherical. The polar groups of the surfactants are in the periphery and the hydrocarbon chains are oriented toward the center, forming the core of the micelles

Inverted spherical micelles:

In solvents of low polarity or oils micelles are inverted. The polar groups face inward to form the core of the micelle while the hydrocarbon chains are oriented outward

Cylindrical and lamellar micelles:

In more concentrated solutions of surfactants, micelles change from spherical either to cylindrical or lamella.

Factors Effecting CMC:

Temperature affects the CMC of surfactant as temperature increases CMC of ionic surfactants decreases. The CMC are higher for ionic than nonionic surfactants. The charges in the micelle of ionic surfactant are in close, to overcome the resulting repulsion an electric work is required but nonionic surfactants have no electric repulsion to overcome in order to aggregate. Electrolytes also effect the CMC of ionic surfactants the addition of salt in ionic surfactants reduces the electric repulsion between charged group and lower CMC values. Branched chain system and double bond raises the CMC the chains must come together inside the micelles. The increase in chain length of hydrocarbon facilitates the transfer from aqueous phase to micellar phase which causes decrease in CMC. The greater intraction with water retard micelles thus ionic surfactants have high in polar solvent than nonionic surfactants.

Incompatibilities of Surfactants:

Non Ionic Surfactants:

Nonionic surfactants have few incompatibilities with drugs and are preferred over ionic surfactants. These surfactants form weak complexes with some preservatives as phenols, including esters of p-hydroxybenzoic acid (Parabenzes) and with acids like benzoic and salicylic via hydrogen bonds. This reduces the antibacterial activity of these compounds.

Ionic Surfactants:

Ionic surfactants are capable of reacting with compounds possessing ions of the opposite charge. These reactions may bind the surface active ions, sometimes resulting precipitation. The compounds which react with active ions of surface are also changed and this is harmful in physiological and pharmacological point of view.

Anionic Surfactants:

Anionic surfactants react with cationic drug causes precipitation or lose in potency or availability of drug. Cationic drugs include Alkaloidal salts, local anesthetics, most sympathomimetic, cholinomimetic, adrenergic blocking, skeletal muscle relaxants, antihistamines, many tranquilizing and antidepressant agents.

Cationic Surfactants:

Cationic surfactants form complexes with water soluble Polymers containing negatively charged group such as natural gums Acacia, agar, carrageenan, taragacanth, alginate, sodium carboxy methyl cellulose and carbopol.

Lecture 25

Viscosity

Viscosity is defined as the resistance in flow of a substance. A substance with high viscosity is thick and trouble flowing for example honey while a liquid with low viscosity is thin and flows easily e.g. water. Similarly high viscosity lava flow slowly and cover a small area. In contrast low viscosity magmas flow rapidly and forms lava that cover thousands of square kilometers. Viscosity is very important in study of plastic material. Viscosity of plastic material is very important and depends upon environmental factors. Plastic material does not behave as many other liquids do when these are in molten state. As we increase the temperature of plastic the polymer chains become enlarge causes them to high viscosity due to which they cannot flow easily. As we increase the temperature the viscosity of the material decreases because things expand on heating.

Fluid Dynamics:

It is the branch of fluid mechanics which deals with the flow of fluids. To understand about fluid dynamics we have to discuss about following items:

1. Reynolds number
2. Turbulent and laminar
3. Newtonian and non-Newtonian fluids
4. Fountain Flow

Reynolds Number:

Reynolds number is used to make prediction similar flow pattern in different fluid dynamic situation. There are two distinct types of flow turbulent and laminar flow. Turbulent flow is very random and there is a lot of mixing that takes place within molecules while laminar flow is very ordered and molecules flow in layers. Reynolds number is a dimensionless number means a number which represents a physical quantity but not measured on the scale of physical units or do not have any unit such as π.

Reynolds number and Turbulent Flow:

The Reynolds number (Re) of a fluid moving through a round channel is equal to

$$\mathrm{Re} = \frac{\text{density} \times \text{velocity} \times \text{diameter}}{\text{viscosity}} = \frac{\rho \times v \times d}{\mu}$$

If has a Re less than 2300 then it shows laminar flow from round channel and if Re is in between 2300-4000 the fluid shows transitional flow and if it is greater than 4000 the fluid shows turbulent flow from round channel.

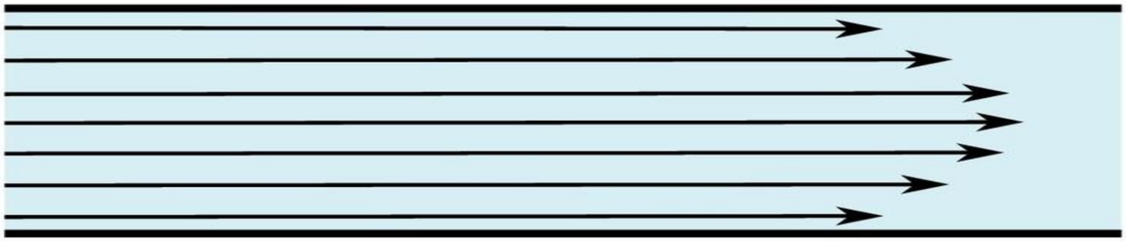
Turbulent Flow:

Turbulent flow provides a higher degree of mixing and a more consistent temperature across the flow channel than laminar flow. In applications where we use water flow to cool tooling; we want turbulent flow in order to get better heat transfer.

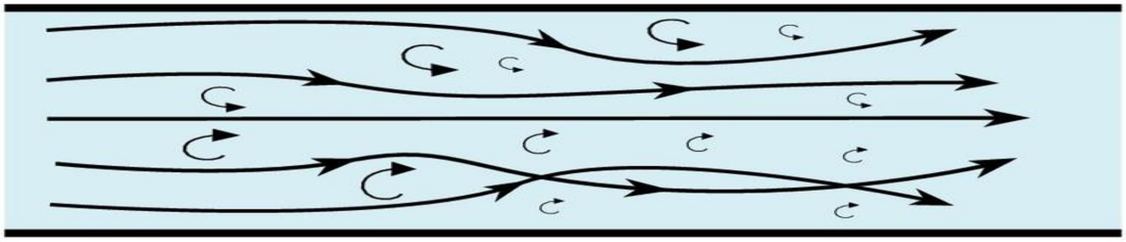
Laminar Flow:

Turbulent flow is very chaotic and there is a lot of mixing that takes place, Laminar flow is much smoother and there is a difference in velocity across the flow channel. The molecules at the channel wall are flowing more slowly than the molecules in the middle due to frictional drag. Laminar flow is sometimes envisioned as a series of plates or layers that flow across each other. If each laminate can be assumed to be moving at a constant velocity then the number of laminates will be determined by the thickness of the flow channel, the average velocity, and the viscosity of the liquid. The shear rate (the rate of change of velocity at which one layer of fluid passes over an adjacent layer) is determined by the velocity divided by the thickness of the laminate or $\gamma = v/h$. where γ is shear rate, v is velocity of fluid while h is thickness of laminate.

laminar flow



turbulent flow



Newtonian Fluid:

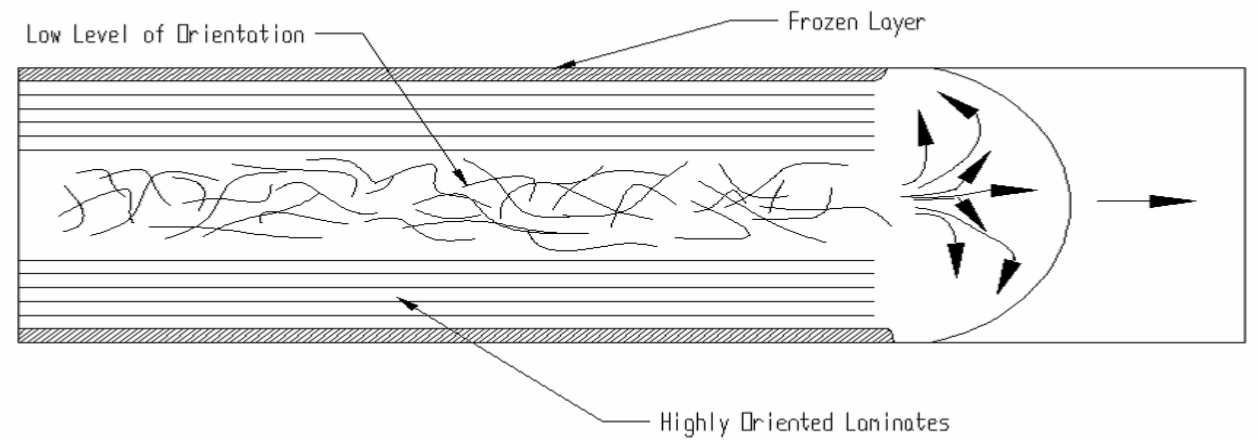
A Newtonian fluid is a fluid that the viscosity stays the same when the shear rate changes. Some examples of Newtonian fluids include water, organic solvents, and honey. For those fluids viscosity is only dependent on temperature

Non Newtonian Fluid:

In reality most fluids are non-Newtonian, which means that their viscosity is dependent on shear rate the viscosity of these fluids drop as shear rate is increased.
A good example of this behavior is with ketchup, when the ketchup is just sitting in the bottle, it is at a high viscosity and difficult to get to flow, once it starts flowing the tomato fibers align and it flows more easily.

Fountain Flow:

When plastic molecules flow into a cold mold in order to make a component, they exhibit fountain flow due to their high viscosities and high aspect ratios (width to height ratio). The molecules in the middle of the flow channel remain in a relatively amorphous arrangement (without form) with a low level of orientation. The molecules at the mold wall freeze in place almost instantly. The molecules just inside of the frozen layer see the highest shear rate.



This phenomenon of fountain flow allows for operations like in-mold decoration, where a decal is placed into a mold and the plastic is injected over it. The plastic does not race across the mold face, it lays down similar to if paint rollers were traveling across it.

Advantages of Viscosity:

1. High viscosity inhibits the crystal growth.

2. High viscosity prevents the transformation of metastable crystal to stable crystal.

3. High viscosity enhances the physical stability**.**

Disadvantages of viscosity:

1. High viscosity hinders the re-dispersibility of the sediments

2. High viscosity retards the absorption of the drug.

3. High viscosity creates problems in handling of the material during manufacturing