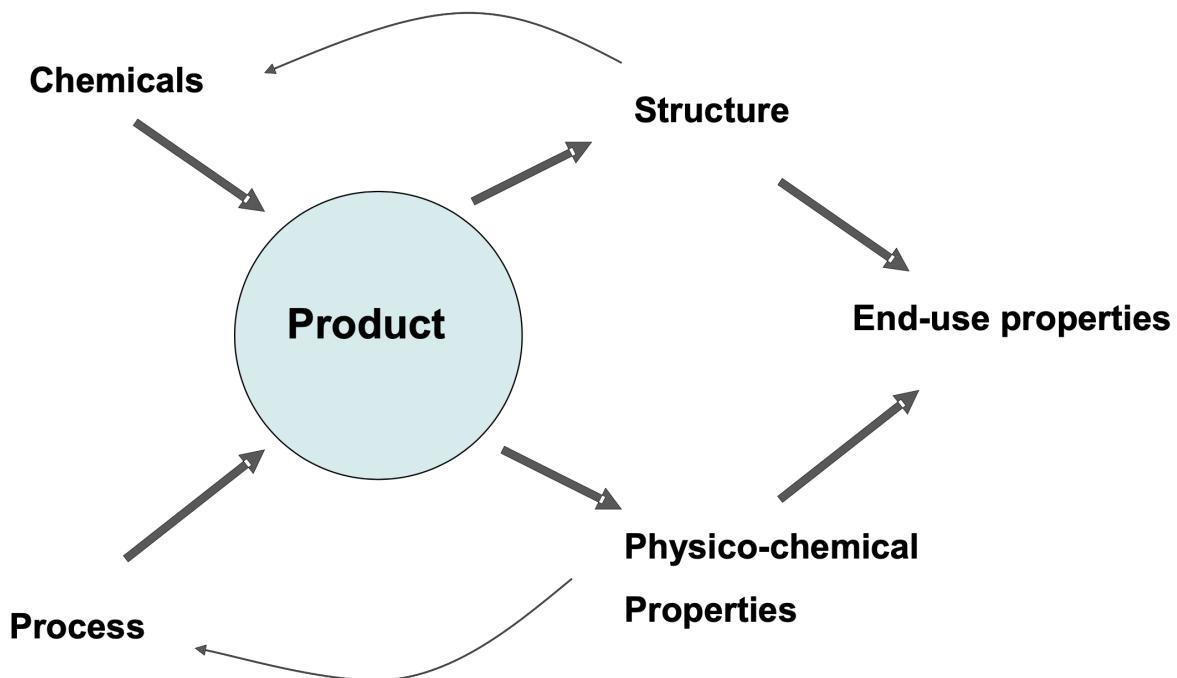


# 1. Rheology

In the context of modern process industries, such as those involved in the production of foods, pharmaceuticals, personal care products, advanced materials, and other formulated products, a comprehensive understanding of the critical engineering and chemical attributes of the final product is indispensable for effective product development and optimisation. To achieve this, a diverse range of characterisation techniques has been developed to interpret and analyse experimental data, and understanding the applications, limitations and benefits of these techniques is crucial for accurate and reliable product characterisation. It is therefore the objective of this course to introduce state-of-the-art experimental techniques for product characterisation, including rheology, spectroscopy, thermal analysis and surface analysis, and identify the most appropriate characterisation technique for a given product.



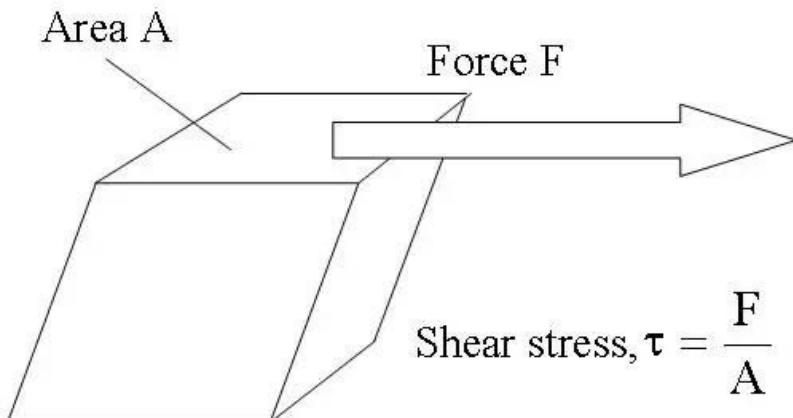
## Introduction to Rheology

Rheology is a field of study that focuses on understanding the flow and deformation behaviour of materials. Whether it is during the processing or end-use application of complex fluids, the rheological properties of a material can have a significant impact on its overall performance. Negative attributes such as unpleasant mouthfeel in foodstuffs, poor levelling in paints or coatings, and settling of particulates on storage in emulsions can all be attributed to specific rheological responses. This highlights the importance of understanding the link between the functionality of a material and its flow properties.

## Basic Definitions

### Shear Stress

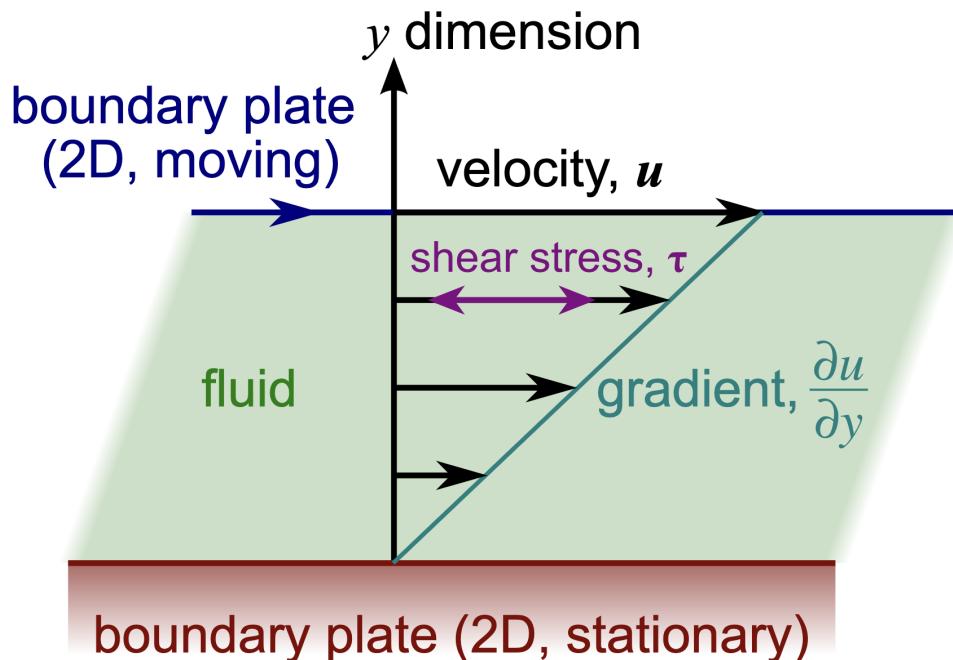
Shear stress ( $\tau$ ) is the force that causes deformation of a material by slippage along a plane or planes parallel to the applied stress. This type of stress can occur in both solids and liquids, with the latter being related to fluid viscosity.



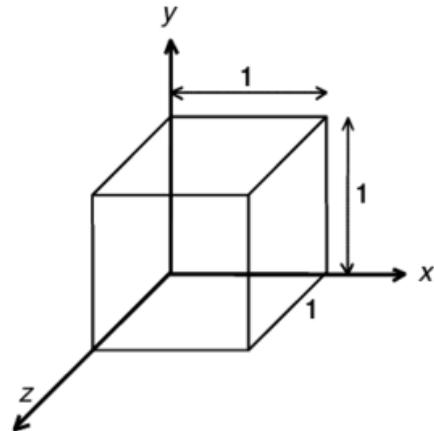
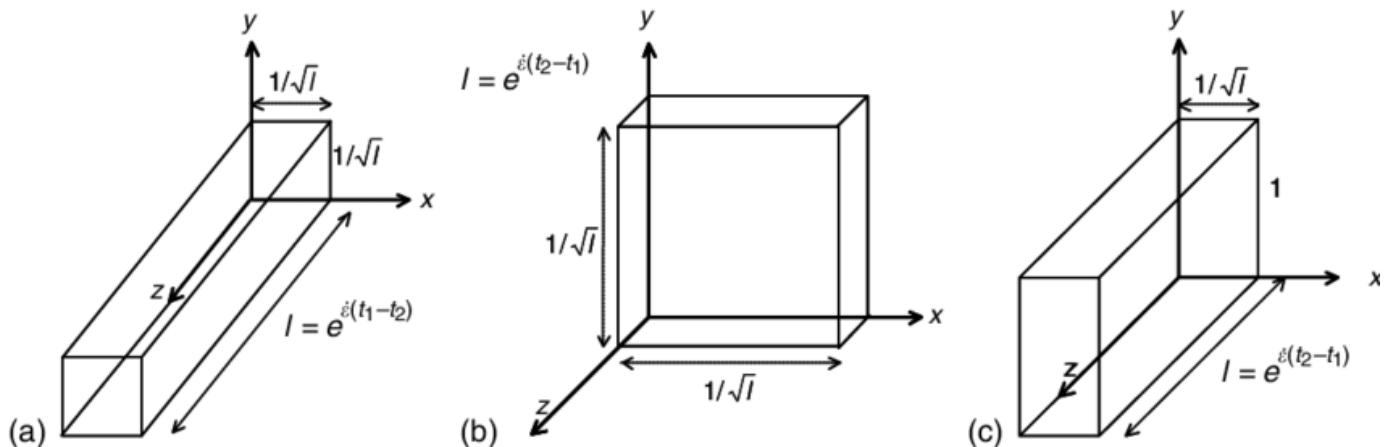
## Flow Regimes

The rheological behaviour of materials is highly sensitive to the type of deformation they experience. Generally, there are three flow regimes that materials can undergo:

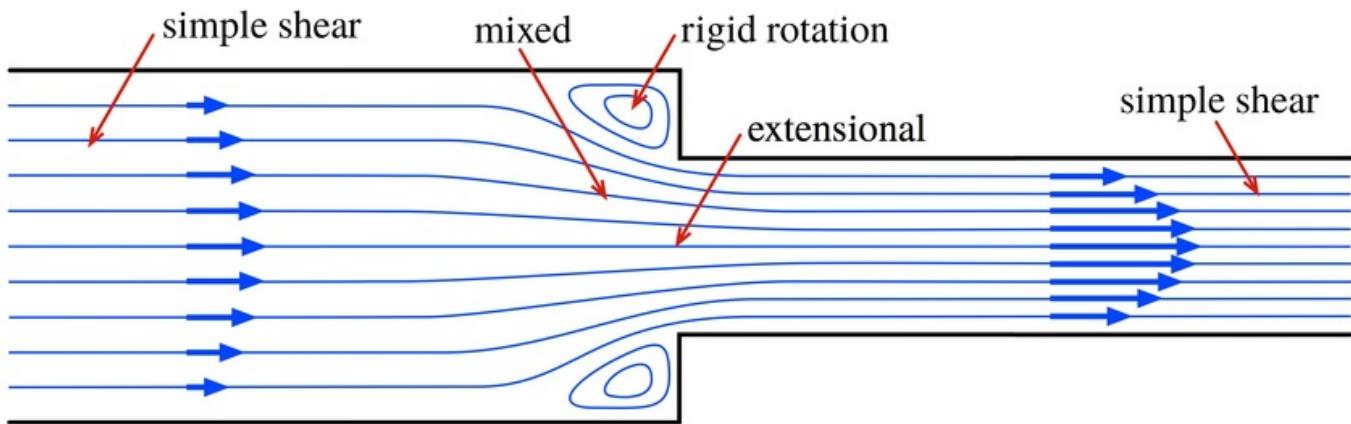
- ▶ Shear flow: this refers to the deformation of a material in response to an applied shear stress. When a material is subjected to a shear stress, the layers of the material slide over each other, causing deformation. Couette flow is a type of shear flow, where the material flows between two infinite, parallel plates that are separated by a distance  $h$ , with one plate moving with a constant velocity  $u_0$  in its own plane, while the other plate remaining stationary.



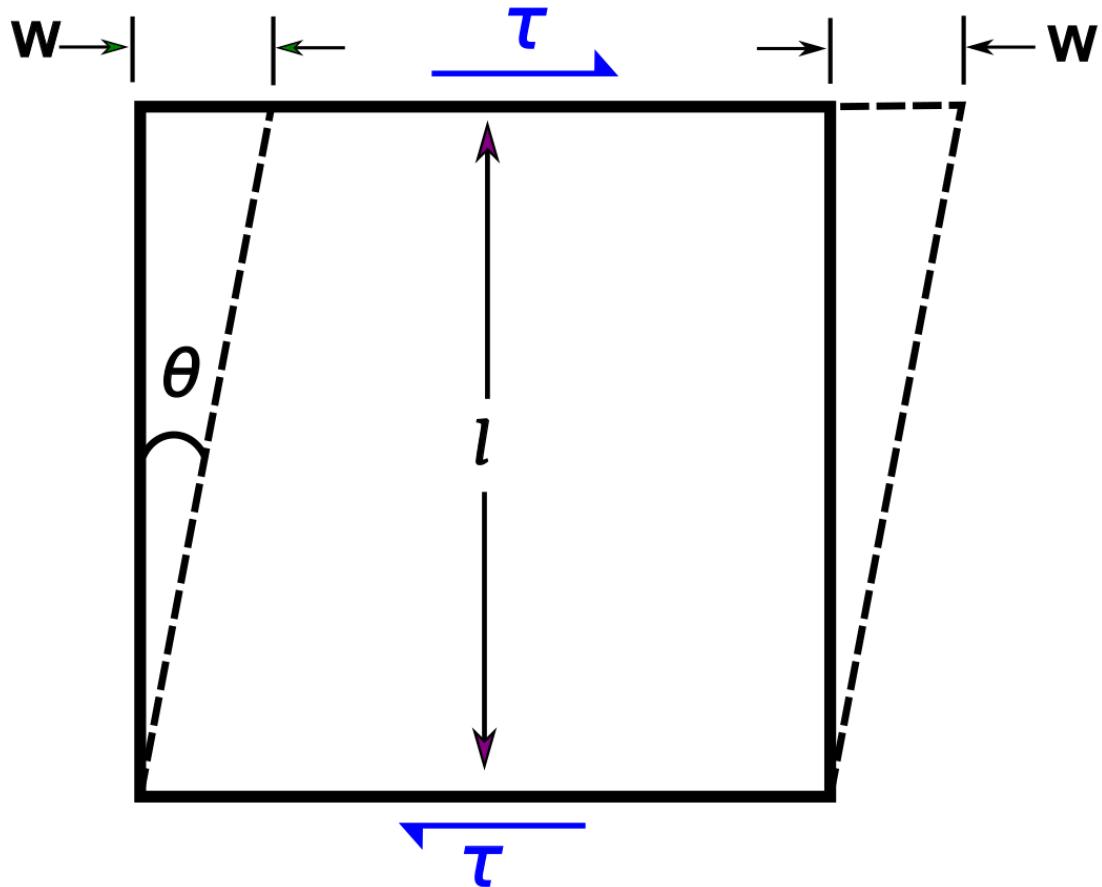
- ▶ Extensional flow: this refers to the deformation of a material in response to an applied extensional stress, which causes the material to elongate or stretch. Unlike shear flow, which involves the sliding of adjacent layers of material, extensional flow involves the stretching of the material itself in a direction perpendicular to the applied stress.

**Undeformed****Deformed**

- Complex flow: this involves both shear and extensional deformation, and is thus more difficult to study and model because the combination of deformation modes can give rise to complex interactions between different parts of the material. Complex flow can occur in many industrial flows, such as ram extrusion, flow through narrow channels or porous media, the deformation of materials under high strain rates, and the deformation of viscoelastic materials under both shear and extensional stresses.

**Shear Strain**

Shear strain ( $\gamma$ ) is a measure of relative deformation in a material, which can be defined differently depending on the type of deformation. In a shear deformation, strain is determined by dividing the distance moved in the direction of the deformation by the height of the unit that was deformed. In an extensional deformation, the strain is more simply defined as the length of the material before deformation divided by the length after deformation.



$$\text{Engineering shear strain } \gamma = \frac{w}{l} = \tan(\theta) \approx \theta$$

## Strain Rate

Strain rate (or shear rate,  $\dot{\gamma}$ ) is defined as the rate at which the fluid is moving relative to the walls of the container divided by the gap between the walls of the container. The units of strain rate are typically 1/sec. In other words, the strain rate measures the amount of deformation occurring in a fluid due to the applied shear stress over a specific time interval.

## Viscosity

Viscosity ( $\eta$ ) is a fundamental property of fluids that determines their resistance to flow when subjected to an applied stress. When a fluid is forced to flow by an applied stress  $\tau$ , the viscosity of the fluid  $\eta$ , determines the shear rate  $\dot{\gamma}$  that persists:

$$\eta = \frac{\tau}{\dot{\gamma}}$$

In other words, the viscosity of a fluid represents the internal friction between its layers, and it determines how easily a fluid can flow. A fluid with a high viscosity will resist flow and require a more substantial applied stress to produce a given shear rate than a fluid with low viscosity. The SI unit of viscosity is pascal-seconds (Pa s), and a fluid with a constant viscosity for all applied shear stresses is known as a Newtonian fluid. The viscosities of some common fluids are:

Material	Approximate Viscosity (Pa·s)
Glass	$10^{40}$
Bitumen	$10^8$
Golden Syrup	$10^2$
Glycerine	1
Olive Oil	$8 \times 10^{-2}$
Mercury	$2 \times 10^{-3}$
Water	$10^{-3}$
Acetone	$3 \times 10^{-4}$
Air	$2 \times 10^{-5}$

## Elasticity

Elasticity is a fundamental property of solid materials that determines their ability to deform under the application of a stress and return to their original shape upon stress removal. When a solid element is subjected to a shear stress  $\tau$ , it experiences a shear strain  $\gamma$ . The magnitude of this strain is determined by the modulus of the material  $G$ , which has units of pascals (Pa):

$$G = \frac{\tau}{\gamma}$$

When a perfect solid is subjected to a shear stress, it undergoes instantaneous deformation or strain, which persists as long as the stress is applied. However, upon the removal of the stress, the solid undergoes an instantaneous recovery to a state of zero strain, and no flow has occurred. The moduli of some common solids are:

Material	Approximate Shear Modulus (MPa)
Diamond	$4 \times 10^5$

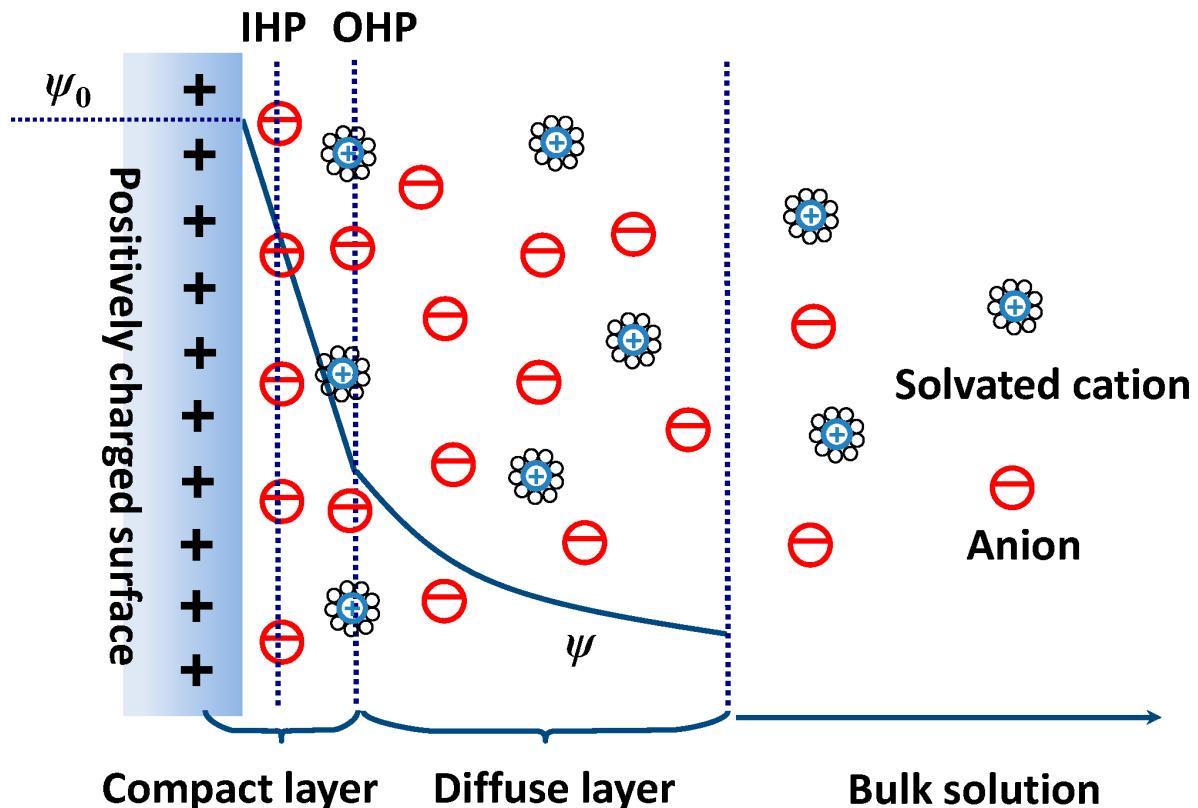
Material	Approximate Shear Modulus (MPa)
Iron and Steel	$8 \times 10^4$
Glass	$3 \times 10^4$
Granite	$2 \times 10^4$
Concrete	$10^4$
HDPE, Nylon	$4 \times 10^2$
Lead	8
Rubber	3
Kitchen Sponge	$2 \times 10^{-2}$

The modulus can also be interpreted as a measure of the material's stiffness and can be used to determine its mechanical properties.

## Rheological Behaviour

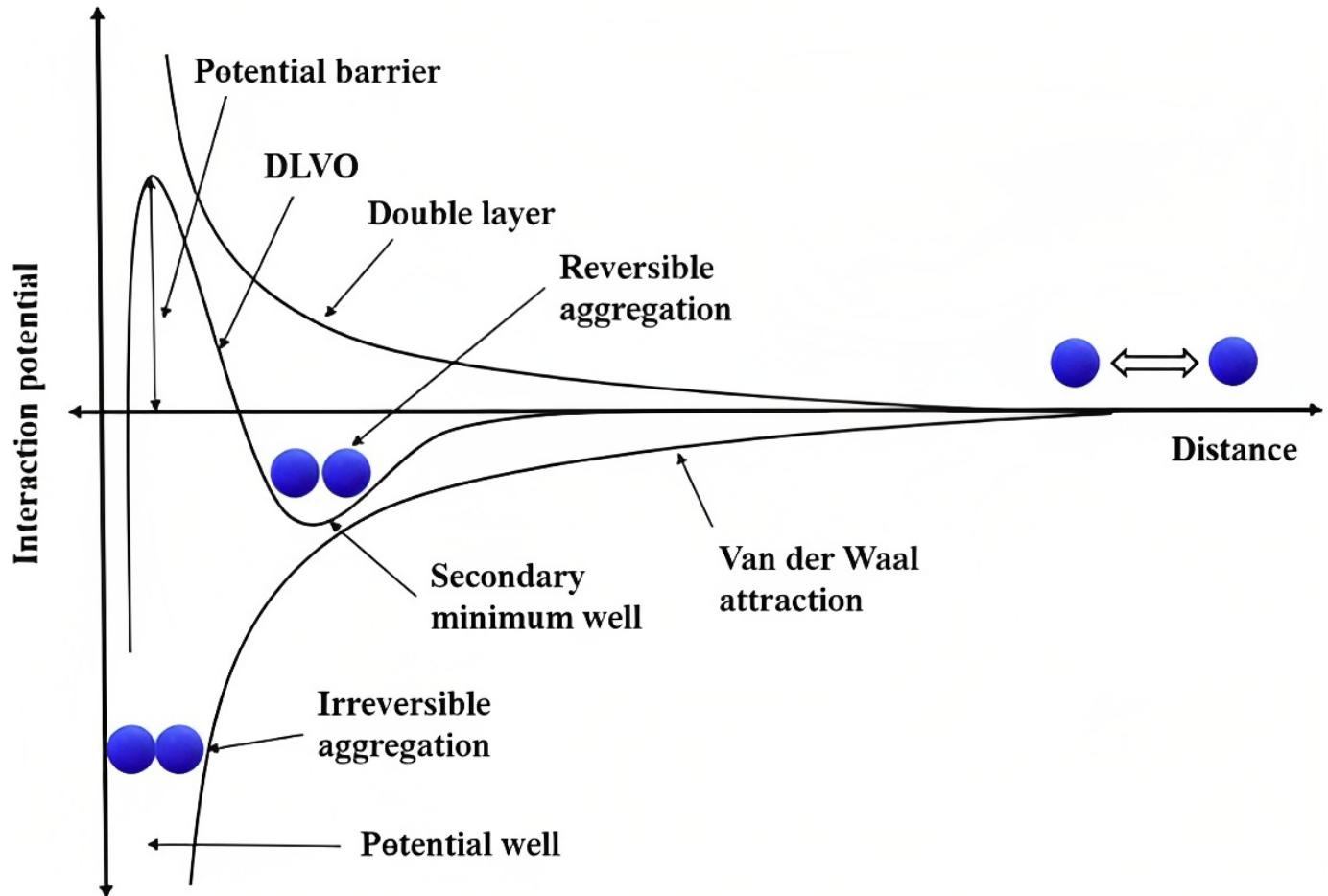
### Interactions Between Charged Particles

Charged particles can play an important role in rheology as they can interact with each other and with the surrounding environment in various manners, which affect the rheological property of the system. For example, in the case of colloidal suspensions, the interactions between charged particles can lead to the formation of aggregates or clusters, which can affect the rheological properties of the suspension, such as viscosity and yield stress. The charge on particles leads to the formation of an electrical double layer (EDL) in solution, which consists of two layers of ions: a compact layer of counterions that are adsorbed to the surface and a diffuse layer of ions that surround the compact layer.



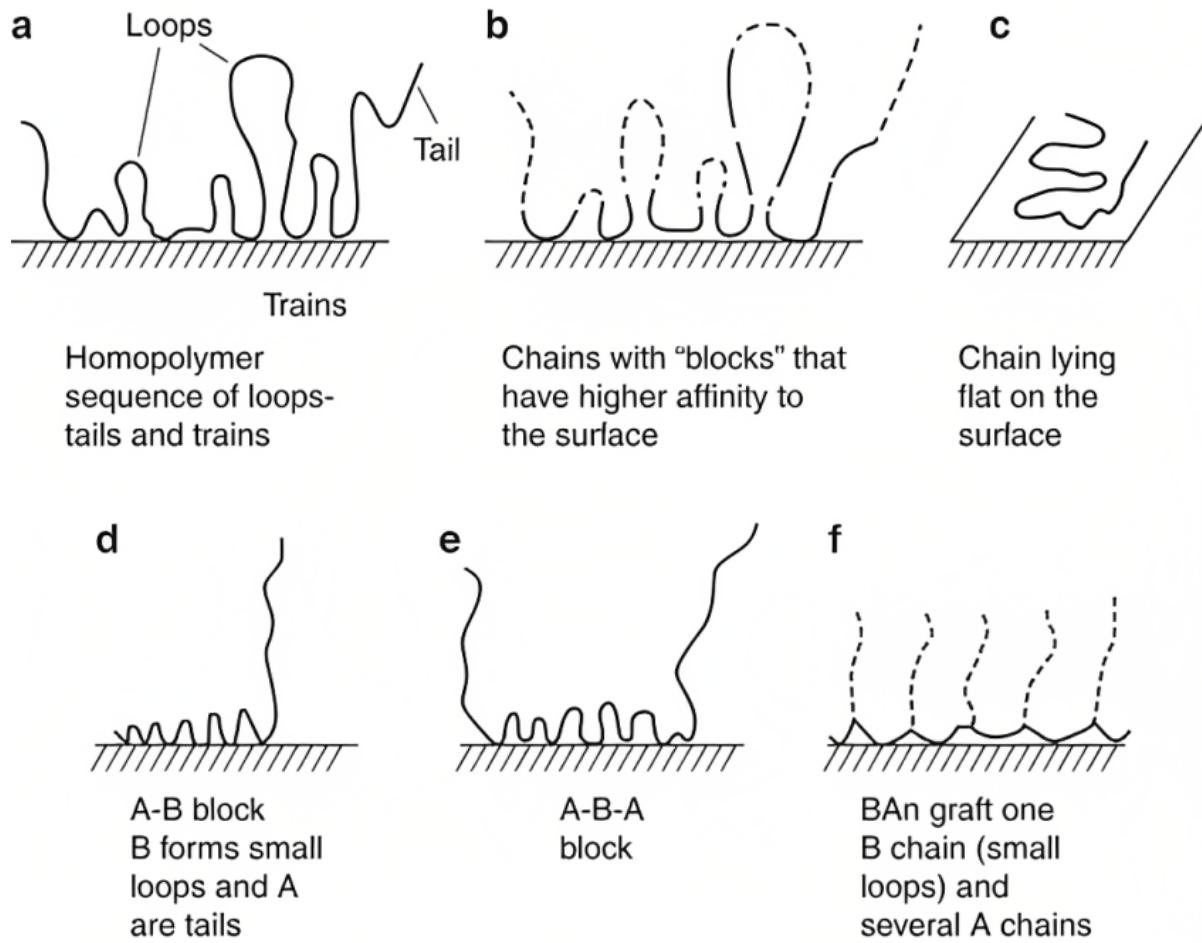
The electrostatic repulsions and van der Waals attractions are two types of intermolecular forces that can contribute to the formation and stability of the EDL. The former consists of the repulsive interaction between the charged surface of the solid particle and the counterions in the diffuse layer of the EDL. The latter arises from the interaction between fluctuating dipoles, which includes London–dispersion, Debye, and dipole–dipole forces. When two particles are extremely close to each other, each particle becomes polarised by the electron cloud of the neighbouring particle, which leads to attractive interaction, thereby keeping the particle together. Therefore, the double layer force stabilises the suspension, while van der Waals force promotes coagulation.

The well-established Derjaguin-Landau-Verwey-Overbeek (DLVO) theory describes the overall particle interactions. The theory is based on the assumption that the electrostatic double layer forces and the van der Waals forces are independent and therefore can be superimposed or added at each interacting distance for two particles. Assuming sphere/sphere interactions, the double layer force decays exponentially with separation, while the van der Waals attraction gives a negative term and is an inverse power law function of the particle separation. The electrostatic potential (interaction energy) between two particles as a function of the distance between them is:



The DLVO curve has a non-monotonic behaviour, which consists of a secondary minimum potential well leading to flocculation (particles attracting each other with weak attraction force). If the interaction energy of this secondary minimum is on the order of the thermal energy ( $kT$ ), then those particles can stick to each other and form aggregates/flocs. The aggregated structure plays a role in the rheological suspension behaviour, such as viscoelasticity and yield structure. However, the interaction between particles at the secondary minimum is weak, and adhesion is reversible. When particles approach even closer proximity, they start to feel a potential energy barrier that will keep particles from touching each other, thus leading to stabilisation due to electrostatic force. The height of the barrier defines the stability of the colloidal system. If external energy is applied to the system using shear, then some particles may overcome the potential energy barrier and enter the primary energy minimum. Once particles are in this potential well, it may be challenging to pull them apart unless very high shear energy is applied, such as sonication, to separate the two primary particles.

An additional complication arises if the assumption of spherical particles is lifted. When a polymer adsorbs onto a surface, it creates a layer of charges on the surface, which can interact with the charges of the electrical double layer around a charged particle. The polymer chains can extend away from the surface and into the surrounding fluid, affecting the stability and behaviour of colloidal suspensions. In particular, the polymer segments can act as steric barriers, preventing the particles from approaching each other and interfering with each other before van der Waals forces play a significant role and aggregate the particles. This steric stabilisation mechanism is often referred to as the "polymer brush" effect and is a critical factor in controlling the stability and rheological properties of colloidal suspensions.



## Rheological Behaviour of Real Materials

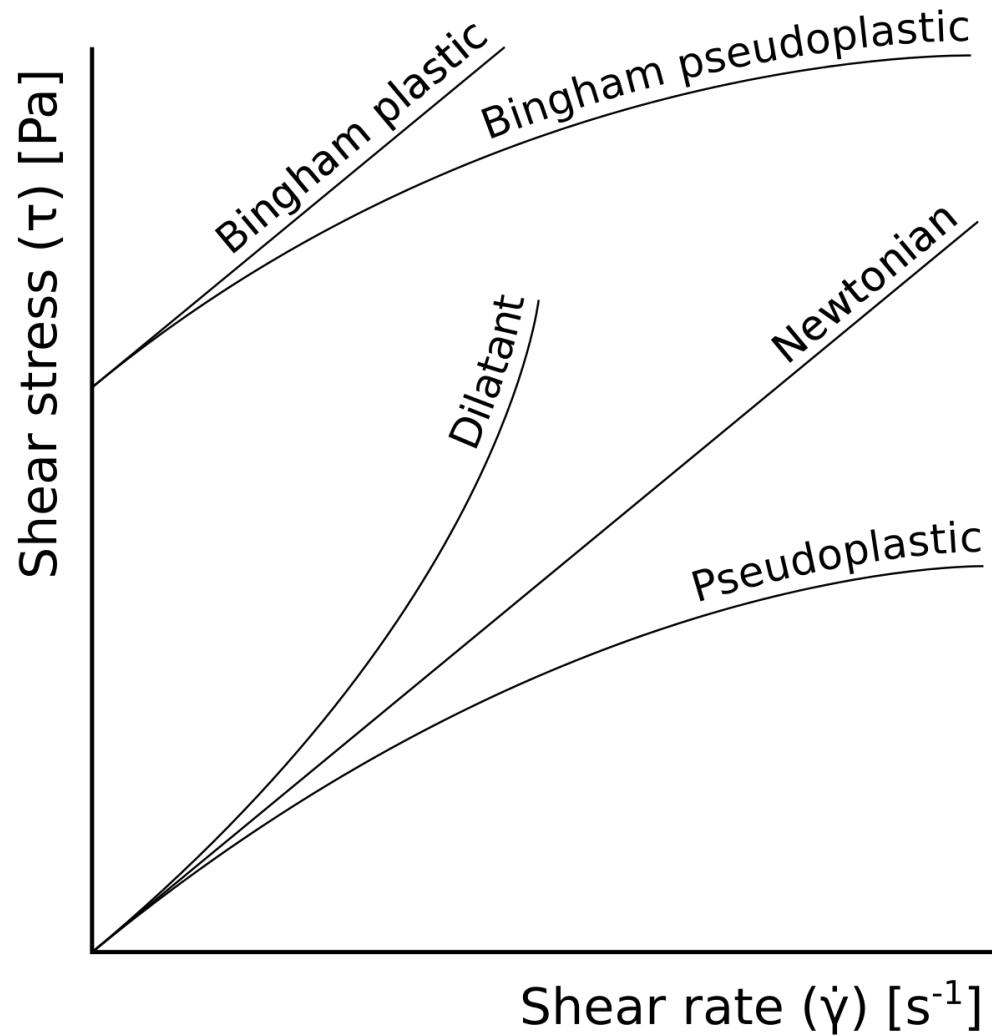
The rheological behaviour of materials is not only sensitive to the type of deformation they experience, as previously addressed, but can also vary depending on their composition and physical properties. Simple fluids, such as Newtonian fluids, are composed of small molecules and follow Newton's law of viscosity. They exhibit constant viscosity regardless of the shear rate or the applied force. Newtonian fluids cannot regain their original shape or form once the applied force is removed. In contrast, Hookean solids are materials that possess a continuous elastic structure, meaning they return to their original state after deformation, characterised by its modulus.

Real materials are complex mixtures of various components, including liquid phases that contain solid particles, liquid droplets, polymer molecules, or surfactants. Their flow and deformation behaviour is a complex combination of viscous (liquid-like) and elastic (solid-like) properties. Viscoelasticity is the term describing such materials that exhibit both viscous and elastic behaviours.

Non-Newtonian fluids, such as Bingham plastics, pseudoplastic fluids, dilatant fluids, and Bingham-pseudoplastic fluids, exhibit varying behaviours when subjected to an external force.

- ▶ Bingham plastics require a minimum amount of stress before they will start to flow and exhibit a constant viscosity at shear rates below the yield stress. Examples of Bingham plastics include clay, grease, asphalt, chocolate and toothpaste.

- ▶ Pseudoplastic (shear-thinning) fluids exhibit decreasing viscosity as the shear rate increases. This means that the fluid will flow more easily at higher shear rates, and it may even appear to be thinning out or becoming less viscous. Examples of pseudoplastic fluids include paints, inks, and some types of polymer solutions.
- ▶ Dilatant (shear-thickening) fluids exhibit increasing viscosity as the shear rate increases. This means that the fluid will become thicker and more resistant to flow as the shear rate increases. Examples of dilatant fluids include corn starch and water mixtures and some types of quicksand.
- ▶ Bingham-pseudoplastic fluids combine aspects of both Bingham plastic and pseudoplastic behaviours. This means that the fluid exhibits a yield stress, like a Bingham plastic, but its viscosity also decreases as the shear rate increases, like a pseudoplastic fluid. Examples include drilling mud, cement slurries, and certain food products like ketchup, mayonnaise, and toothpaste.



## Rheometers

Rheometers are instruments used to determine the rheological properties of materials. Rheometers work by deforming a material in a controlled manner and measuring its response. There are two main types of rheometers: controlled strain and controlled stress.

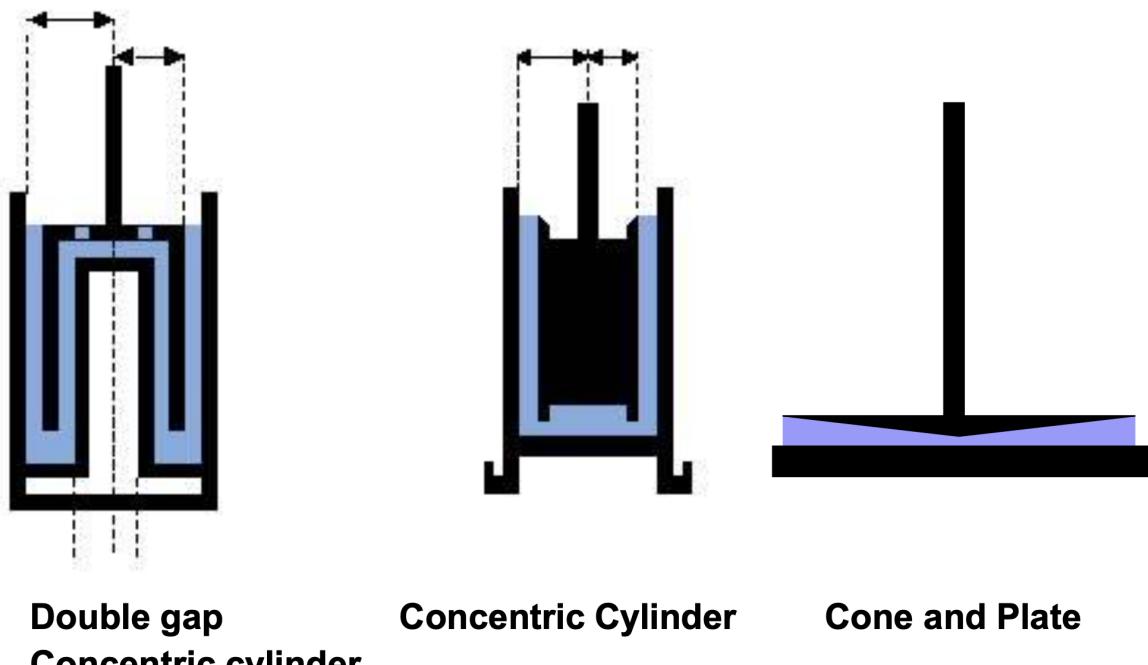
- ▶ In a controlled strain instrument, the material is subjected to a forced deformation, which results in a stress being transmitted through the material that can be measured by some means.

- In contrast, in a controlled stress instrument, the material is subjected to a controlled stress, and the resultant deformation is recorded.

Both types of rheometers allow for slightly different experiments to be conducted. Most modern rheometers are controlled stress instruments. However, many top-of-the-range instruments can perform both types of measurement effectively.

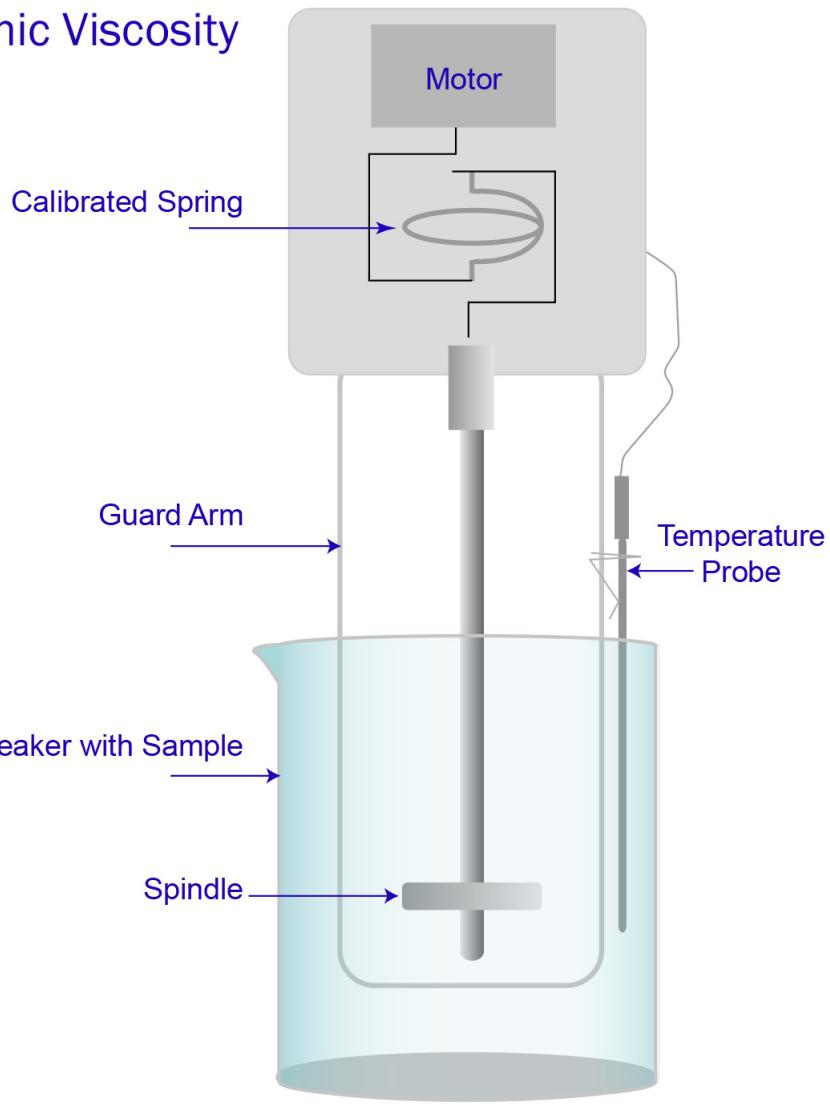
Some practical examples of rheometers include:

- Rotational rheometer: this is where the sample is placed between two parallel plates, with one plate fixed and the other rotating at a controlled speed. The applied torque, or stress, is controlled by the rotational speed of the moving plate and can be varied over a wide range. As the plate rotates, the sample is sheared and deformed, and the resulting stress and strain are measured. Rotational rheometers can be further classified into double gap concentric cylinder, concentric cylinder, and cone and plate:



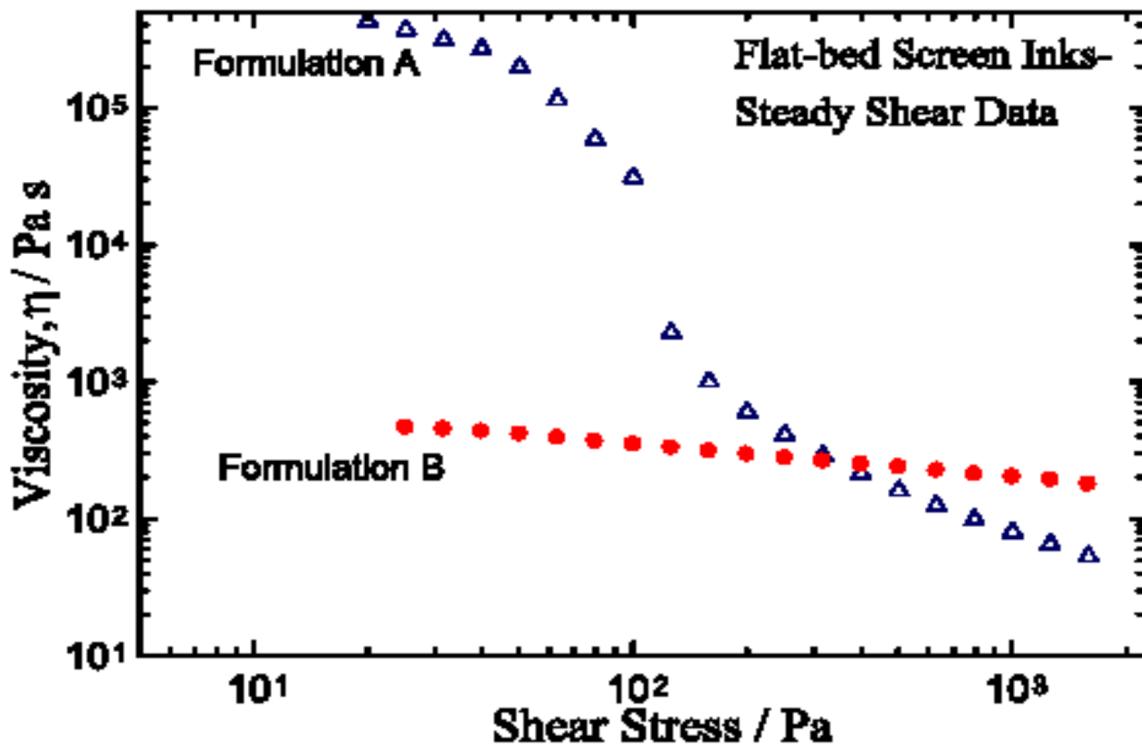
- Brookfield viscometer: this works by applying a rotational force to a sample and measuring the resulting torque required to maintain a constant rotational speed. The resulting viscosity of the fluid can then be calculated using the measured torque and the geometrical characteristics of the instrument. However, because the spindle geometry is fixed, the resulting deformation is relatively constant and can be considered as controlled strain, while the measured torque is proportional to the stress, making it a controlled stress instrument. Therefore, Brookfield viscometer is not strictly a controlled strain or controlled stress instrument, but a hybrid between the two. The Brookfield viscometer offers several advantages, including ease of use and cost-effectiveness.

## Dynamic Viscosity



## Viscometry: Large Strain, Steady Shear Measurements

These measurements are also referred to as viscometric or steady state viscosity measurements, where the objective is to measure the viscosity of a material as a function of either the applied stress or shear rate. At each stress, the sample is continuously sheared in one direction, leading to large strain deformations. An equilibrium value for the viscosity can be obtained by looking at the equilibrium region where the slope of the strain against time curve is linear giving a constant shear rate. The steady state viscosity is then the applied stress divided by the equilibrium shear rate, and the apparent viscosity can then be plotted as a function of the applied shear stress or the measured shear rate to obtain a flow curve. This flow curve provides essential information about the material's behaviour during flow. For example,



Based on the observed data, it can be deduced that Formulation A exhibits weak aggregation, and that the application of a shear stress causes the interactions between particles to break down, resulting in increased flow and a corresponding decrease in viscosity. Conversely, Formulation B demonstrates a relatively high degree of particle stability, which accounts for the minimal change in viscosity in response to shear stress.

## Flow Behaviour Models

Furthermore, fitting measured viscometric data to appropriate models can provide valuable insights into the flow behaviour of a material. One common approach is to use a model that describes the viscosity as a function of shear rate.

### Power Law

In this model, the relationship between shear stress  $\tau$  and shear rate  $\dot{\gamma}$  is described by a power law function of the form:

$$\tau = k\dot{\gamma}^n$$

Hence, the viscosity is:

$$\eta = k\dot{\gamma}^{n-1}$$

where  $k$  is a proportionality constant and  $n$  is the flow behaviour index.  $n$  is a measure of the material's non-Newtonian behaviour, with values ranging from 0 (Newtonian) to 1 (shear-thinning), and above 1 (shear-thickening).



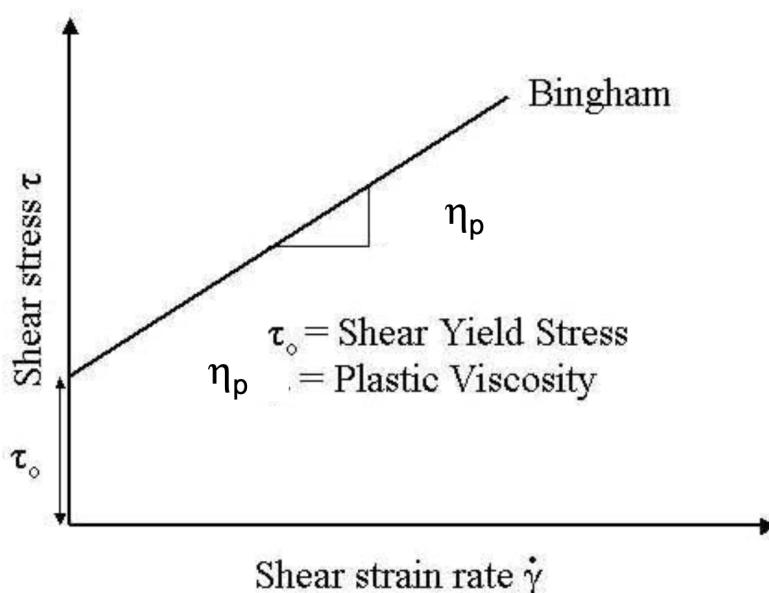
## Bingham Model

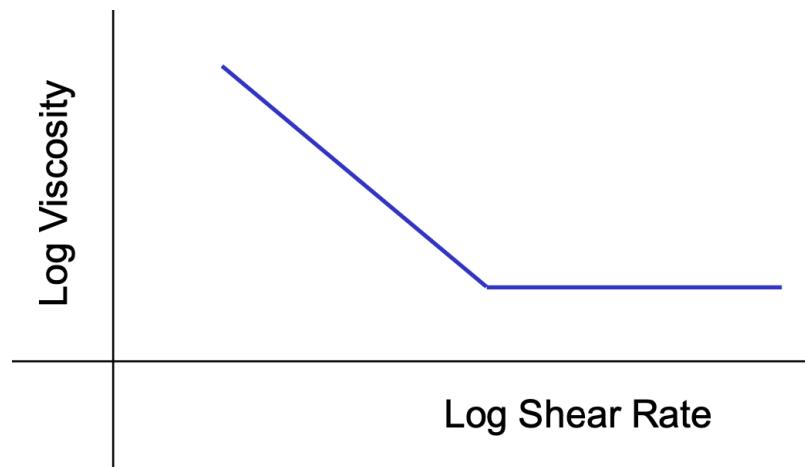
The Bingham model can be used to characterise Bingham fluids, or the flow behaviours of materials that exhibit a yield stress. Yield stress is the minimum stress required for the material to begin flowing, and is a characteristic property of many complex fluids, such as suspensions, pastes, and gels. In the Bingham model:

$$\tau = \tau_B + \eta_p \dot{\gamma}$$

$$\eta = \frac{\tau_B}{\dot{\gamma}} + \eta_p$$

where  $\tau_B$  is the yield stress and  $\eta_p$  is the Bingham viscosity. The Bingham viscosity represents the slope of the linear portion of the flow curve after the yield stress has been exceeded.





The Bingham model is useful in analysing the flow behavior of materials that exhibit both elastic and viscous properties, such as drilling fluids and toothpaste. The model is also particularly valuable in predicting the behavior of materials during start-up and stoppage of flow, as well as in predicting the pressure required to initiate flow. However, the Bingham model cannot capture shear-thinning behavior, which is common in many complex fluids.

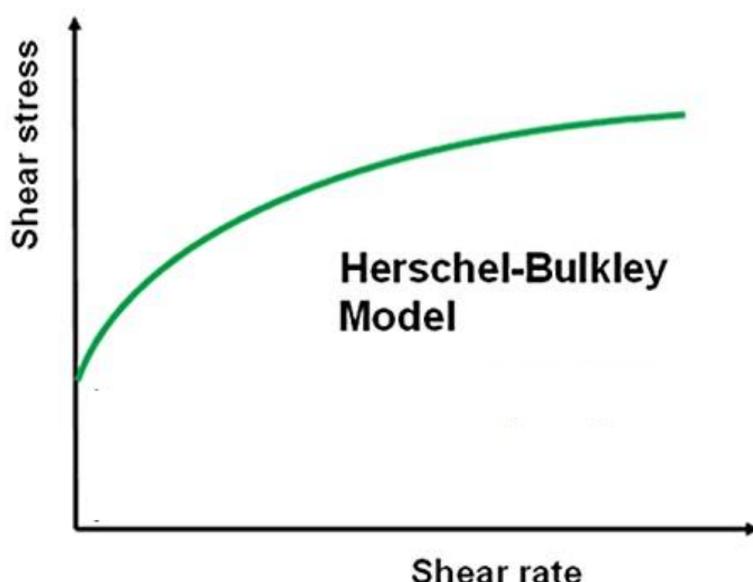
### Herschel-Bulkley Model

The Herschel-Bulkley model is essentially a combination of the power law and the Bingham model:

$$\tau = \tau_{HB} + k\dot{\gamma}^n$$

$$\eta = \frac{\tau_{HB}}{\dot{\gamma}} + k\dot{\gamma}^{n-1}$$

where  $\tau_{HB}$  is the yield stress,  $k$  is a consistency index, and  $n$  is the flow behaviour index. The consistency index represents the slope of the linear portion of the flow curve, and the flow behaviour index is a measure of the degree of shear thinning.



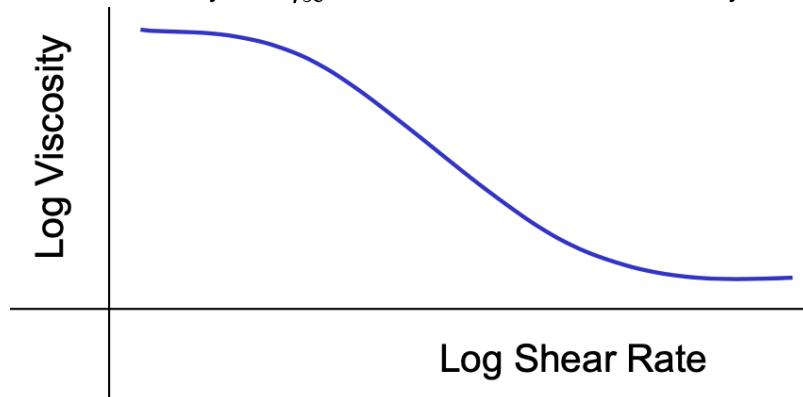
The Herschel-Bulkley model can be useful in analysing the flow behavior of a wide range of materials, including polymers, paints, and food products, but it assumes that the material's flow behavior is independent of time and temperature, which may not always be the case in practice.

## Cross Model

Finally, the Cross model is characterised by a shear thinning region linking a low shear limiting viscosity and a high shear limiting viscosity:

$$\eta = \eta_\infty + \frac{\eta_0 - \eta_\infty}{1 + (k\dot{\gamma})^m}$$

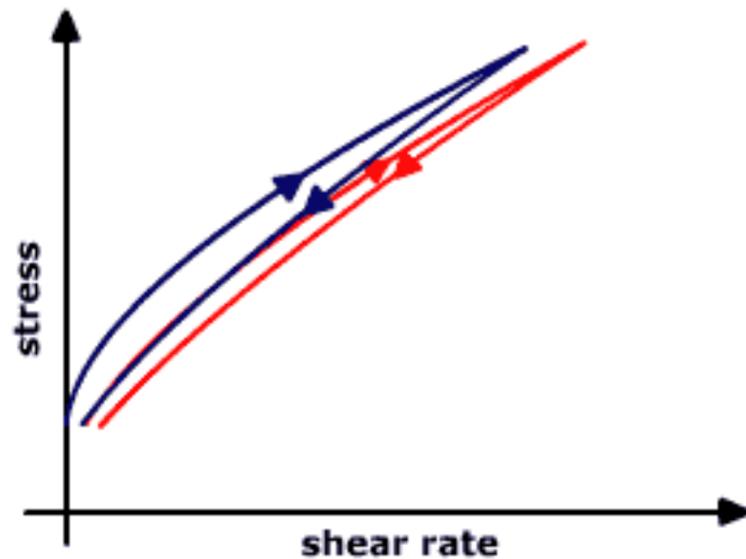
where  $\eta_0$  is the zero-shear-rate viscosity and  $\eta_\infty$  is the infinite-shear-rate viscosity.



The Cross model is particularly useful in analysing the flow behaviour of polymeric fluids, such as solutions and melts, and can provide valuable insights into the effect of molecular weight and concentration on the flow properties of these materials. It is also useful in predicting the behaviour of materials during processing, such as extrusion or injection moulding. However, again, the Cross model assumes that the material's flow behaviour is independent of temperature. Additionally, the Cross model can be difficult to fit to experimental data, particularly when the material's flow behaviour is complex.

## Thixotropy

Thixotropy is the tendency of a material to recover structure lost during shear, either after the cessation of shear, or as the shear stress or shear rate is reduced. Thixotropy is a reversible process that occurs in many different types of materials, including gels, pastes, and some types of fluids. One of the ways in which thixotropy is observed experimentally is in the difference between the viscosity measured as the stress is increased (up sweep) with the viscosity recorded as the stress is then reduced (down sweep).



The important thing to understand about thixotropy is the rate at which the material recovers its structure and the difference between the structure before and after shear. This is usually the case in real applications, where the material structure has been broken down and is then required to structure when there is no further stress being applied.

The best way to measure thixotropy is to apply a constant shear rate to the material for a set time, and monitor the structure recovery is using a non-invasive low strain oscillation measurement.

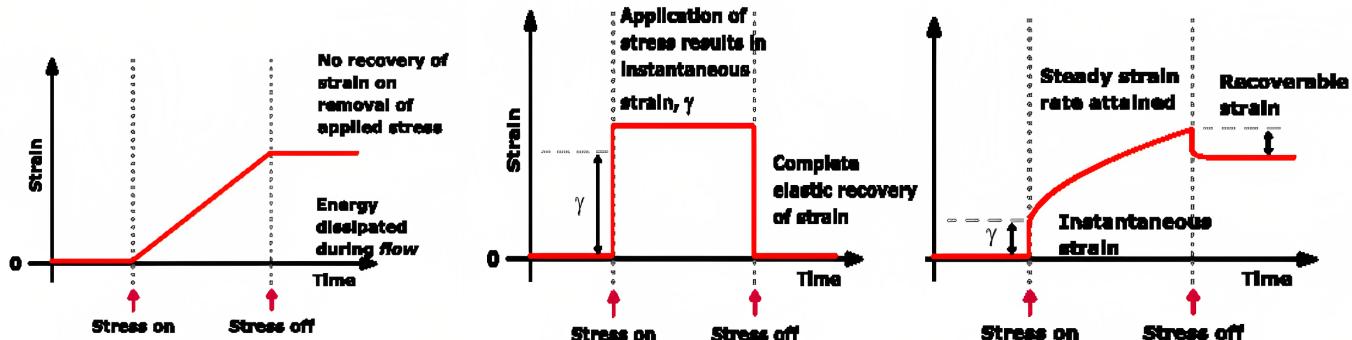
## Small Strain Measurements

As just mentioned, small strain measurements are a technique used to probe the structure of a material by applying very small deformations that do not disrupt the microstructure of the material. In other words, the deformations are so small that they do not cause any permanent changes to the material's structure.

### Constant Stress (Creep)

In a creep experiment, a constant stress is applied for a period of time and the resultant strain is measured during and after the stress has been removed. The strain response will be very different for different materials.

- Newtonian liquid
- Hookean Solid
- Viscoelastic Material



- ▶ Newtonian Fluid: continues to flow and deforms linearly with time. Does not recover upon removal of the applied stress.
- ▶ Hookean Solid: deforms under the constant load, and the amount of deformation will be proportional to the load and will be time-independent. Recovers completely upon removal of the applied stress.
- ▶ Viscoelastic material: initially deform rapidly under a constant load and then slowly approach a steady-state deformation. The amount of deformation over time will depend on the viscoelastic properties of the material. The creep strain observed will typically exhibit a curved or sigmoidal shape, reflecting the time-dependent behavior of the material.

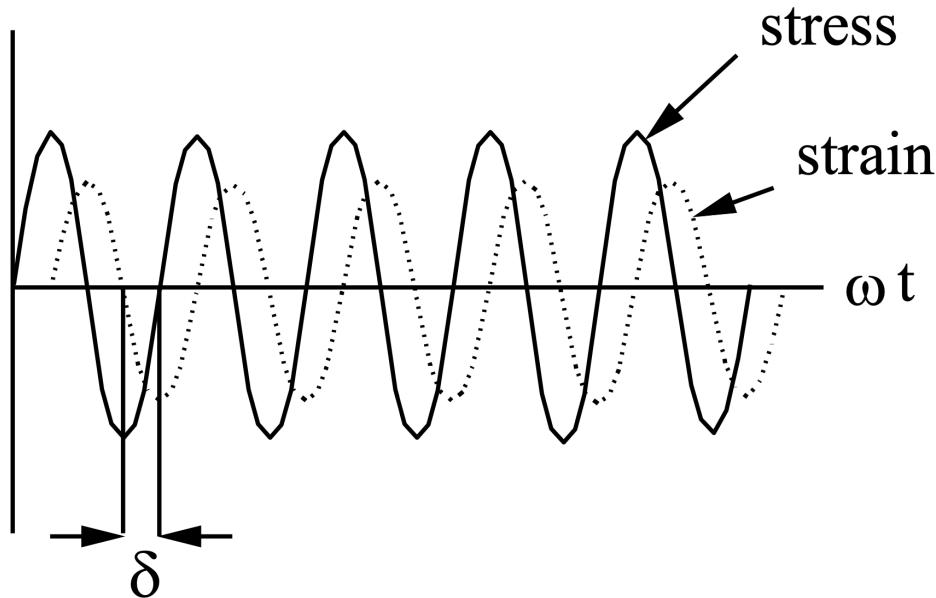
In such experiments, the shear modulus can be determined by dividing the applied stress by the resultant strain, and the viscosity of the material can be obtained by dividing the applied stress by the slope of the linear portion of the strain-time graph. Also, to better understand the balance between the elastic and viscous properties of materials and derive model equations to depict the behaviours, mechanical analogues can be used. For example, a perfectly elastic spring can represent the Hookean elastic response of a material, while the movement of a plunger within a container of Newtonian oil (a dashpot) can represent the viscous flow response to stress.

Finally, yield stress creep experiments can be used to determine the yield stress of a material. This involves performing a series of creep measurements at successive stresses (while leaving an appropriate time for the sample to relax between measurements) and noting the stress at which the material changes from solid-like to liquid-like behaviour. This change is indicated by a constant slope in the compliance/time plot or the failure of the material to recover its original shape after deformation.

## Oscillatory Shear Measurements

In these experiments, a sinusoidal shear stress is applied to the material, and the resulting strain is measured.

Again, the physical justification is that, at low applied stress, the strain amplitude ( $\gamma_0$ ) varies proportionally to the stress amplitude ( $\tau_0$ ) and small strains are non-destructive to the system structure. This proportionality exists only at very low strain amplitudes, and the region in which it exists is known as the linear viscoelastic region. The application of a sinusoidal stress to the sample results in the generation of a sinusoidal deformation. The resultant deformation varies with the same angular frequency,  $\omega$ , and has an amplitude  $\gamma_0$ . The strain wave is shifted out of phase with the stress by an angle,  $\delta$ , the phase angle:



Under linear conditions, the amplitude ratio ( $\tau_0 / \gamma_0$ ) is a characteristic material property that can be used to determine the complex shear modulus ( $G^*$ ). This is a measure of the material's resistance to deformation under shear stress in the linear viscoelastic regime. It is a complex quantity that is made up of two parts: the storage modulus ( $G'$ ) and the loss modulus ( $G''$ ). The storage modulus represents the material's ability to store elastic energy when deformed under shear stress and is in phase with the applied stress. It is a measure of the material's stiffness and is related to its elastic properties.

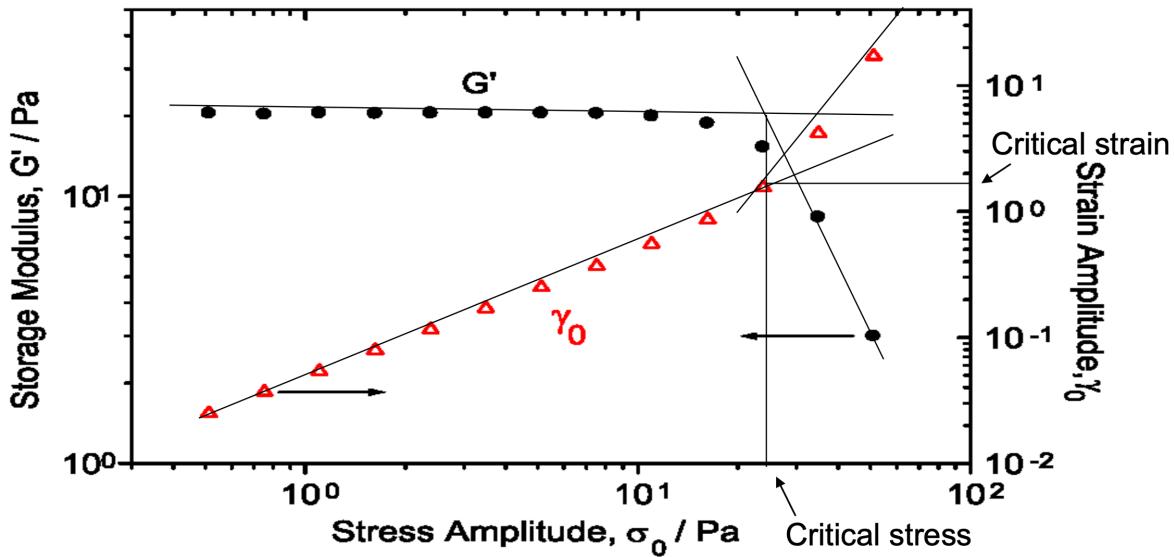
$$G' = \frac{\tau_0}{\gamma_0} \cos \delta$$

The loss modulus represents the material's ability to dissipate energy when deformed under shear stress and is out of phase with the applied stress. It is a measure of the material's viscosity and is related to its viscous properties.

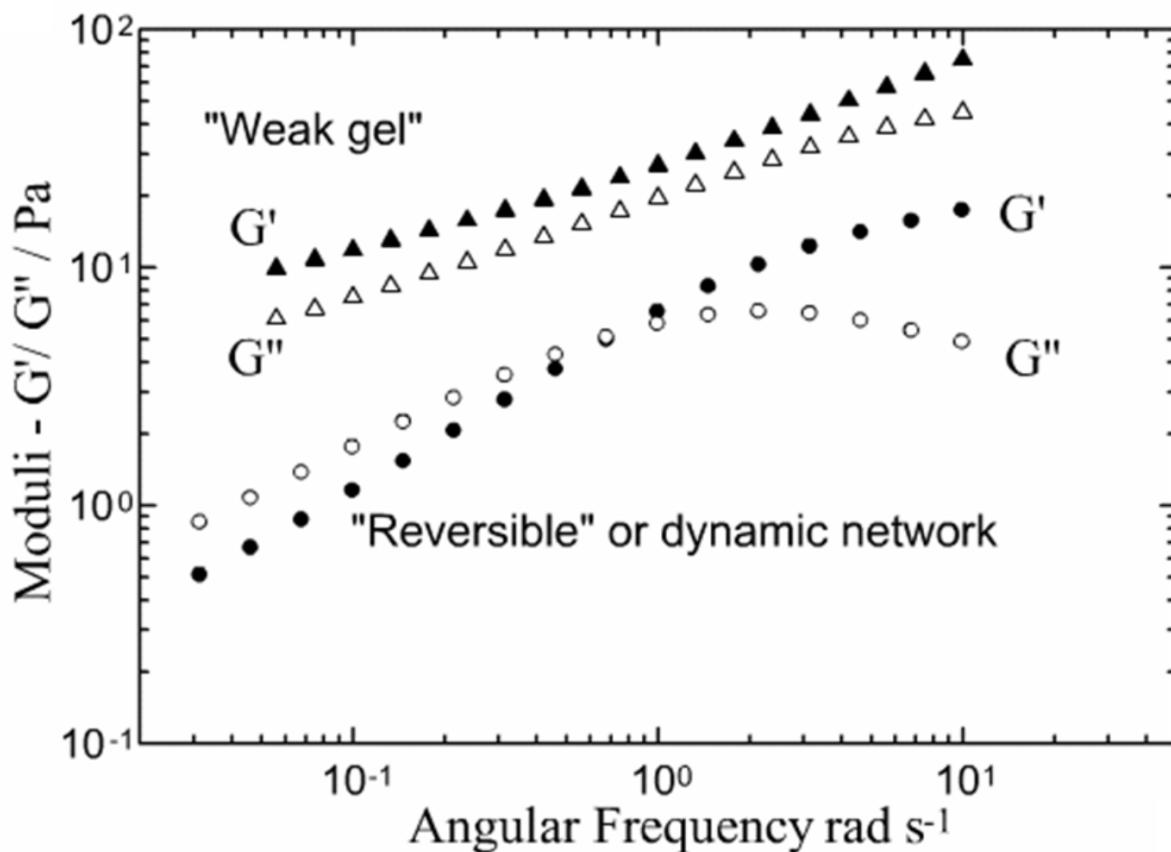
$$G'' = \frac{\tau_0}{\gamma_0} \sin \delta$$

Together, the storage and loss moduli make up the complex shear modulus, and the ratio of the loss modulus to the storage modulus is a measure of the material's damping properties.

Furthermore, the critical strain ( $\gamma_0$ ) defines the point at which the linearity between the stress amplitude and the strain amplitude is lost, which is a material-specific parameter and varies depending on the type of material being tested. For example, typical critical strains for colloidal systems might be  $\gamma_0 < 1.0$  (100 for polymer solutions and  $\gamma_0 < 0.02$  for colloidal dispersions). If we increase the stress amplitude to the point where large deformations are generated, the microstructure will be disrupted. The response will now be non-linear and the value of  $G^*$  and  $\delta$  (and therefore  $G'$  and  $G''$ ) will depend strongly on the value of  $\tau_0$  and will no longer be characteristic of the equilibrium material properties.



Finally, a frequency sweep experiment can provide information about the time scales of stress relaxation in a material. As the frequency of the applied deformation is increased, the material's response changes due to the different timescales of deformation and relaxation involved. At low frequencies, the deformation is applied slowly enough that the material has time to relax and reach equilibrium between cycles. At higher frequencies, the deformation is applied more rapidly, and the material may not have time to fully relax between cycles, resulting in a different viscoelastic response. By probing the structure as a function of frequency in the linear viscoelastic region (i.e. below the critical strain), the balance between elastic and viscous processes at different timescales can be determined.



## Rheology of Dispersions

This is the study of how dispersed particles behave in a liquid or semi-solid medium. The properties and behavior of such systems are largely determined by the interparticle forces that operate within them, which dictate the tendency towards either colloidal stability or flocculation behavior. The interplay between these forces is reflected at a macroscopic level through the rheology of the system. Various types of interparticle forces are at play in dispersions, including attractive forces like the van der Waals force, polymeric depletion flocculation forces, and polymeric bridging flocculation. On the other hand, repulsive forces may arise due to electrostatic repulsion between similarly charged particles or steric interactions between adsorbed polymer layers.

For non-interacting spheres, the simplest description of the viscosity of a dispersion of such particles is given by the Einstein relation, which describes the effective viscosity of the dispersion  $\eta$  as controlled by the volume fraction of the dispersed particles  $\phi$  and the viscosity of the continuous phase (fluid in which the particles are suspended)  $\eta_s$ :

$$\frac{\eta}{\eta_s} = 1 + 2.5\phi$$

The term  $2.5\phi$  represents the contribution of the dispersed particles to the overall viscosity of the system.  $\phi$  is the ratio of the volume of the dispersed phase to the total volume of the system, which is a measure of the concentration of particles in the system. The term  $(1 + 2.5\phi)$  represents the correction factor that takes into account the effect of the particles on the viscosity of the medium. This factor arises from the assumption that the particles move independently of each other and do not interact with each other or with the surrounding fluid.

This equation only holds for dilute dispersions with a volume fraction less than 10%. At concentrations below 20% volume fraction, the Bachelor equation holds well for hard sphere dispersions.

$$\eta_r = 1 + 2.5\phi + 6.2\phi^2$$

This can be extended to a more general form of

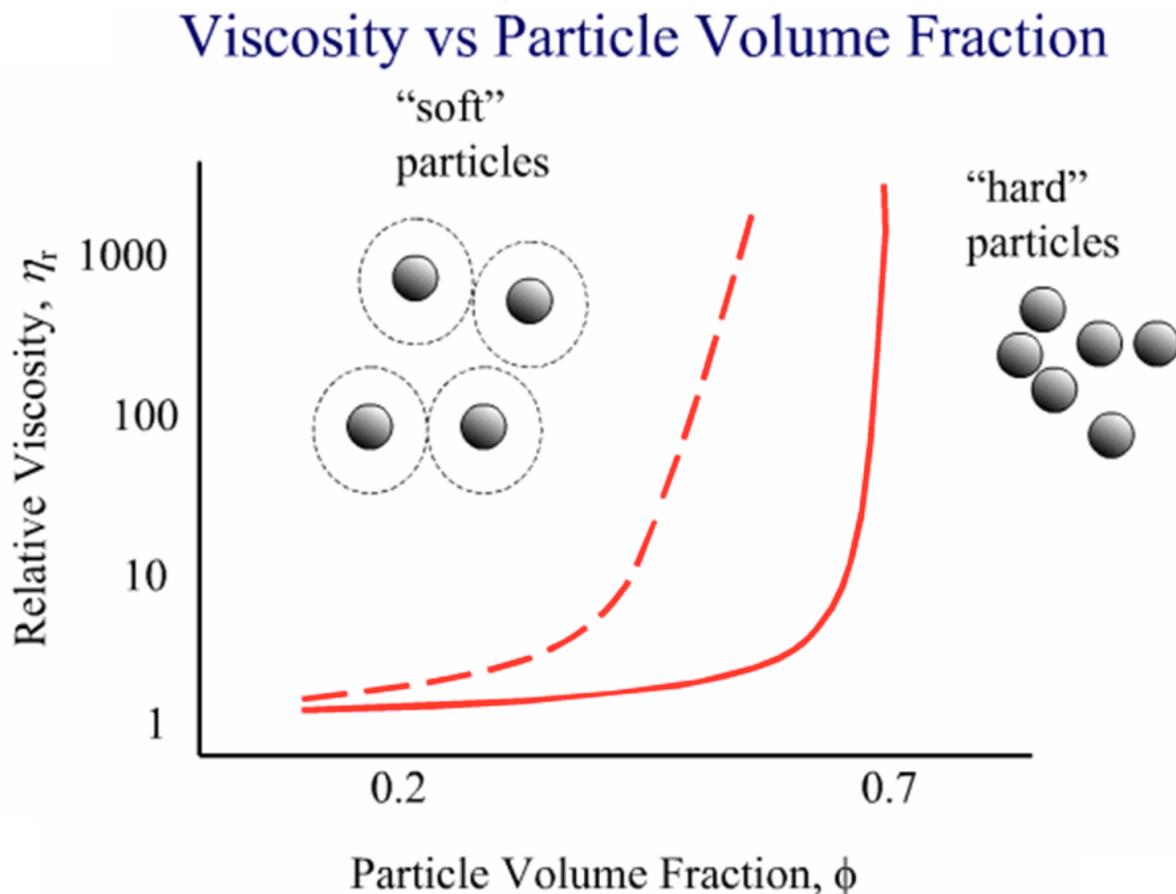
$$\eta_r = 1 + \alpha\phi + \beta\phi^2$$

where values of  $\alpha$  and  $\beta$  have been determined for suspensions of differing particle geometry, but these equations only work up to about 20% by volume.

Experimental observations have commonly shown that  $\eta_r$  increases gradually with increasing volume fraction until a certain critical value, above which the relative viscosity increases sharply. Further increase in the volume fraction of the disperse phase results in a situation in which the particles attain a state of maximum packing. At this point,  $\eta \rightarrow \infty$  and the volume fraction correspond to the maximum packing fraction  $\phi_{\max}$ . This effect is quantified in the Krieger Dougherty equation:

$$\eta_r = \left(1 - \frac{\phi}{\phi_{\max}}\right)^{-[\eta]\phi_{\max}}$$

For interacting particles, the particles can feel each other at longer range than their physical dimensions due to either electrical double layer interactions or adsorbed polymer. This increases the “effective” volume fraction of the particles and hence increases the viscosity:



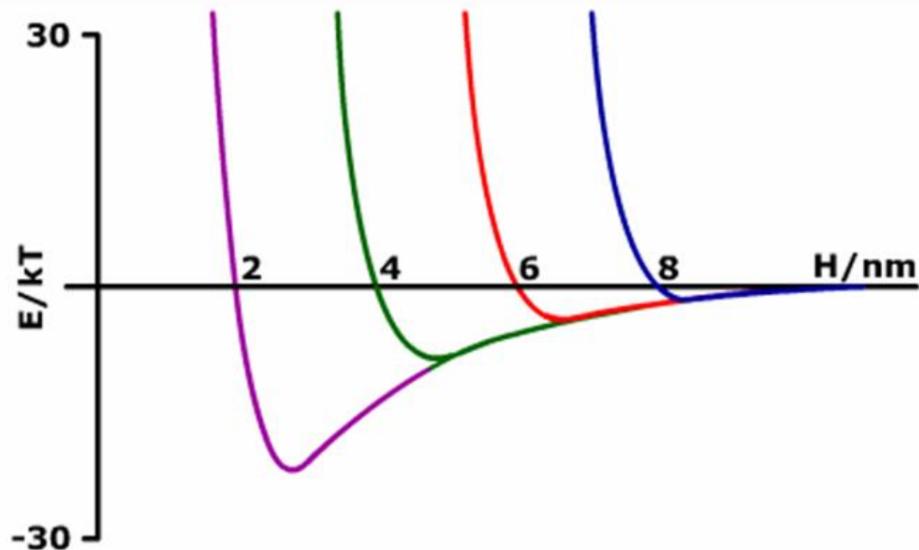
The rheology of these dispersions changes with particle volume fraction. At low volume fractions, the polymer (or double) layers do not interpenetrate and the system is a viscous liquid. However, as the volume fraction increases the layers overlap and compress to give an effective network throughout the system. At this point the system becomes predominantly elastic with  $G'$  (storage modulus) dominating  $G''$  (loss or viscous modulus). This is because the effective network of particles and polymer layers now stores more of the applied energy as elastic energy, rather than dissipating it as heat like the viscous fluid does. This also presents a method of controlling the rheology of a dispersion simply by changing the particle concentration and the nature of the adsorbed polymer layer.

## Flocculated Dispersions

This is where particle-particle interactions predominate, leading to the formation of aggregated networks involving the particulate phase. In these systems, the particles tend to stick together and form larger clusters, or flocs, due to attractive forces such as van der Waals interactions.

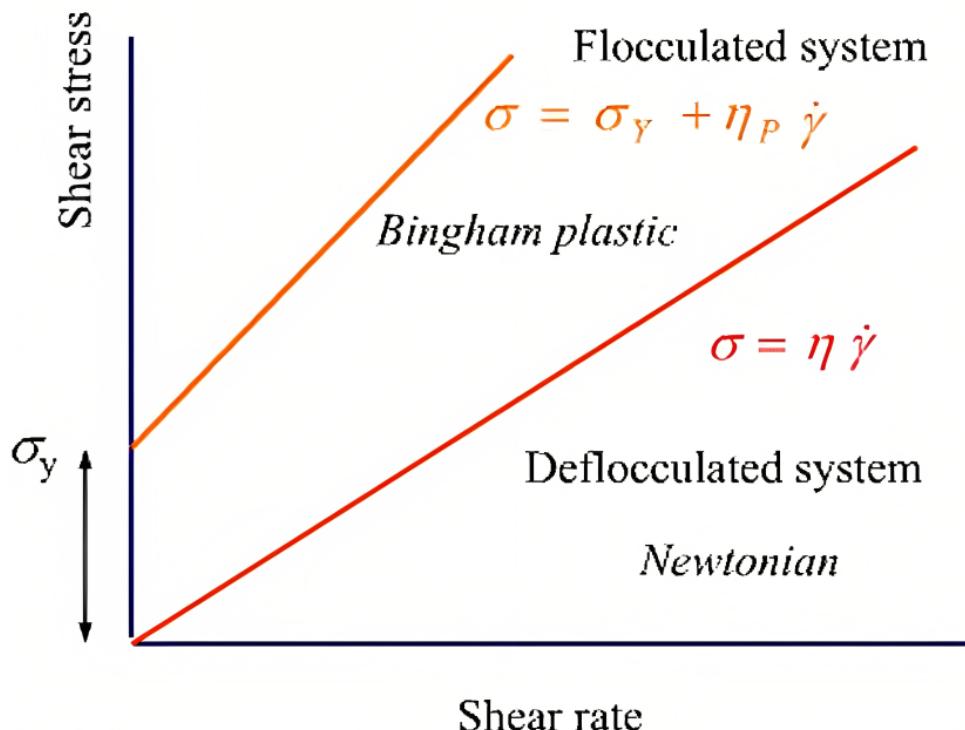
However, in some cases, flocculation may occur at the minimum in the potential energy-distance curve if the thickness of the adsorbed layer surrounding the particles is too low. This means that the particles may come too close to each other, leading to the formation of irreversible aggregates. The adsorbed layer is a layer of molecules, usually polymers or surfactants, that adsorb onto the particle surface and help to stabilise the dispersion by providing steric or electrostatic repulsion between the particles. The potential energy-distance curve shows the energy required to move two particles closer or farther apart from each other, as a function of their separation distance. The curve has a minimum at a certain separation distance, which corresponds to the

most stable distance between the particles. If the thickness of the adsorbed layer is too low, the attractive van der Waals forces between the particles can overcome the repulsive forces generated by the adsorbed layer, causing the particles to flocculate.



The figure shows the potential energy-distance curve for two representative particles, with different thicknesses of the adsorbed layer. The surface separation,  $H$ , is the separation of the bare particle surfaces. The four cases shown in the figure represent different scenarios where the thickness of the adsorbed layer is varied. The curve with the lowest energy minimum represents the case where the particles are most likely to flocculate due to the low thickness of the adsorbed layer.

As the particles in a flocculated dispersion are held together by attractive forces, they tend to form larger clusters or flocs that act as a solid-like network. The presence of this network contributes to the overall stiffness of the system, which is reflected in an increase in the apparent yield stress. The magnitude of the apparent yield stress can depend on a variety of factors, such as the concentration and size of the particles, the strength of the interparticle forces, and the nature of the adsorbed layer.



The increase in the apparent yield stress in flocculated dispersions can have important implications for their processing and application properties. For example, if the material is being pumped or mixed, a higher yield stress can lead to increased energy requirements or processing difficulties. On the other hand, the formation of a solid-like network can also provide beneficial properties, such as improved stability and rheological properties in certain applications.

Thus, the rheology of a dispersion can be controlled by controlling the interactions between the particles. For example, increasing the concentration of particles or the thickness of the adsorbed polymer layer can lead to the formation of a more structured network, which can change the material from a viscous liquid to an elastic solid. Another way is through the use of additives. Particle thickeners, such as clay or very fine silica, can be added to a dispersion to increase its viscosity and yield stress. These thickeners can interact with the particles in the system to create a more structured network, similar to the effect of increasing particle concentration or adsorbed layer thickness. Polymers are another class of additives that can be used to control rheology. Polysaccharides, for example, can interact with particles to form a network or entangle with each other to increase the viscosity and yield stress of the system. Polymers can also act as dispersants, preventing flocculation and maintaining the stability of the dispersion.

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