πάντα ῥεῖ Rheology

Shahrood University of Technology

Non-Newtonian Fluid Mechanics

(Part - II)

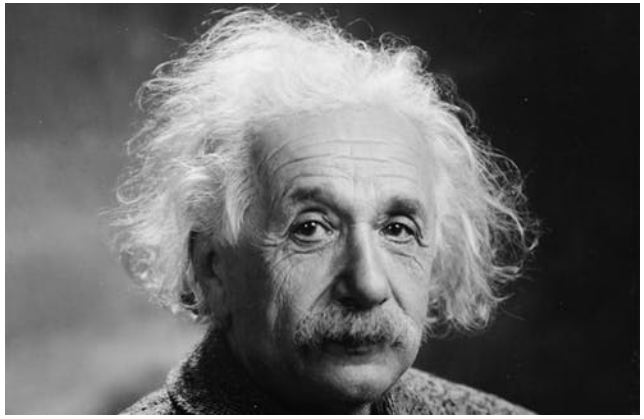
Mechanical Engineering Department,

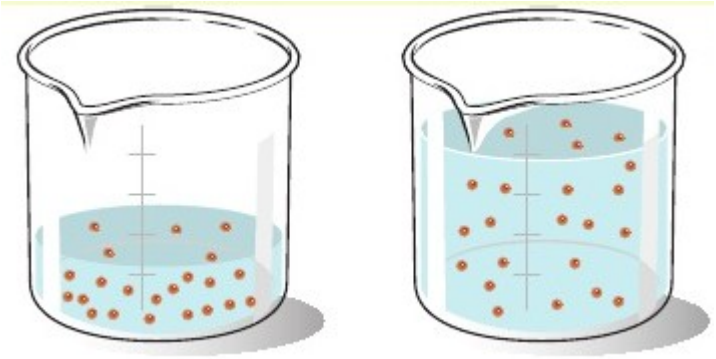
Shahrood University of Technology

By M. Norouzi

April 2021

Viscosity of Newtonian Suspensions



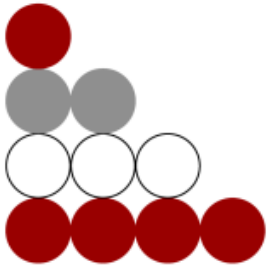
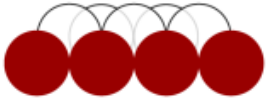
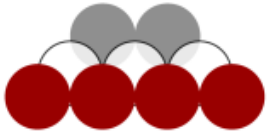
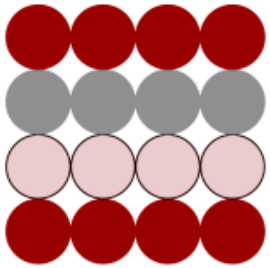
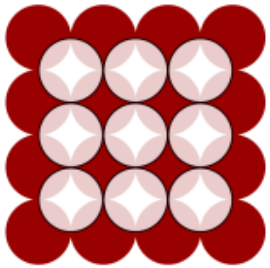
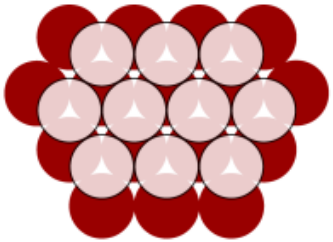
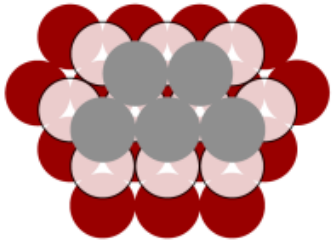


The first major contribution to the theory of the *viscosity of suspensions of spheres* was that of Einstein.[2] He considered a suspension of rigid spheres, so dilute that the movement of one sphere does not influence the fluid flow in the neighborhood of any other sphere. Then it suffices to analyze only the motion of the fluid around a single sphere, and the effects of the individual spheres are additive. The *Einstein equation* is

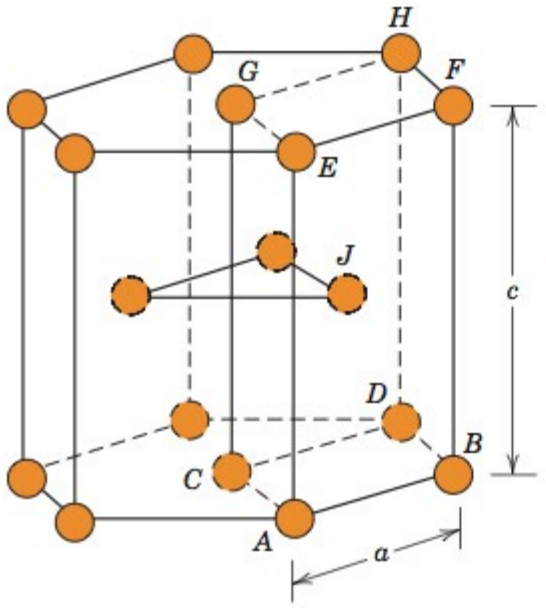
$$\frac{\mu_{\text{eff}}}{\mu_0} = 1 + \frac{5}{2}\phi \qquad (1.6\text{-}1)$$

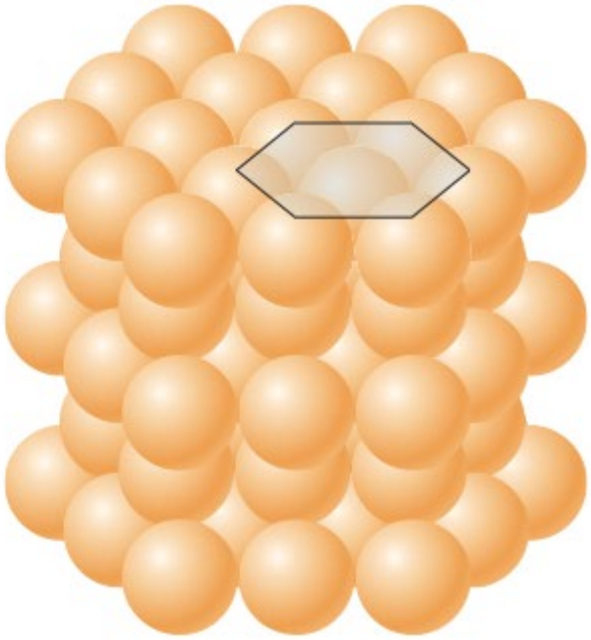
in which μ_0 is the viscosity of the suspending medium, and ϕ is the volume fraction of the spheres. Einstein's pioneering result has been modified in many ways, a few of which we now describe.

Type of Packing of the Spherical Particles

	simple cubic Φ = 0.52	body centered cubic Φ = 0.68	hexagonal close-packed Φ = 0.74	face-centered cubic Φ = 0.74
side view				
top view				

Type of Packing of the Spherical Particles





Hexagonal closet packing of the spherical particles in a concentrated suspensions

Viscosity of Newtonian Suspensions

For *concentrated suspensions of spheres* (that is, ϕ greater than about 0.05) particle interactions become appreciable. Numerous semiempirical expressions have been developed, one of the simplest of which is the *Mooney equation*[7]

$$\frac{\mu_{\text{eff}}}{\mu_0} = \exp\left(\frac{\frac{5}{2}\phi}{1 - (\phi/\phi_0)}\right) \tag{1.6-2}$$

in which ϕ_0 is an empirical constant between about 0.74 and 0.52, these values corresponding to the values of ϕ for closest packing and cubic packing, respectively.

Another approach for concentrated suspensions of spheres is the "cell theory," in which one examines the dissipation energy in the "squeezing flow" between the spheres. As an example of this kind of theory we cite the *Graham equation*[8]

$$\frac{\mu_{\text{eff}}}{\mu_0} = 1 + \frac{5}{2}\phi + \frac{9}{4}\left(\frac{1}{\psi(1 + \frac{1}{2}\psi)(1 + \psi)^2}\right) \tag{1.6-3}$$

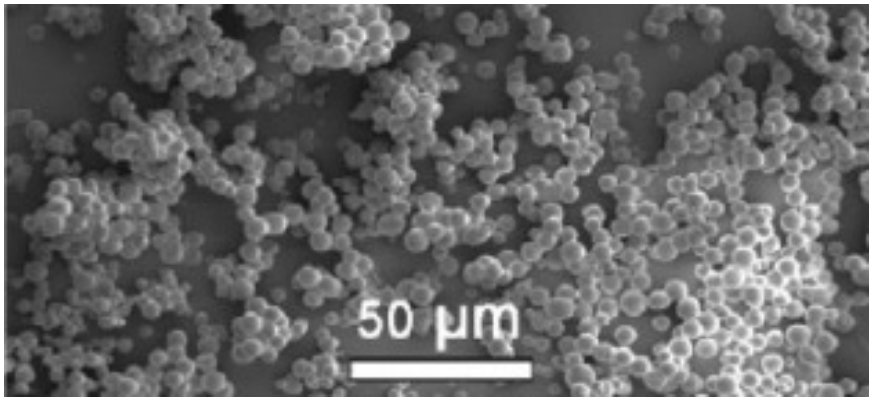
in which $\psi = 2[1 - \sqrt[3]{\phi/\phi_{\max}})/\sqrt[3]{\phi/\phi_{\max}}]$, where $\phi_{\max}$ is the volume fraction corresponding to the experimentally determined closest packing of the spheres. This expression simplifies to Einstein's equation for $\phi \to 0$ and the Frankel–Acrivos equation[9] when $\phi \to \phi_{\max}$.

Viscosity of Newtonian Suspensions

For *concentrated suspensions of nonspherical particles*, the *Krieger–Dougherty* equation[10] can be used:

$$\frac{\mu_{\text{eff}}}{\mu_0} = \left(1 - \frac{\phi}{\phi_{\text{max}}}\right)^{-A\phi_{\text{max}}} \qquad (1.6\text{-}4)$$

The parameters A and ϕ_{max} to be used in this equation are tabulated[11] in Table 1.6-1 for suspensions of several materials.



System	A	ϕ_{max}
Spheres (submicron)	2.7	0.71
Spheres (40 μm)	3.28	0.61
Ground gypsum	3.25	0.69
Titanium dioxide	5.0	0.55
Laterite	9.0	0.35
Glass rods (30 × 700 μm)	9.25	0.268
Glass plates (100 × 400 μm)	9.87	0.382
Quartz grains (53–76 μm)	5.8	0.371
Glass fibers (axial ratio 7)	3.8	0.374
Glass fibers (axial ratio 14)	5.03	0.26
Glass fibers (axial ratio 21)	6.0	0.233

Viscosity of Newtonian Emulsions and Suspensions of Charged Spheres

For *emulsions* or *suspensions of tiny droplets*, in which the suspended material may undergo internal circulation but still retain a spherical shape, the effective viscosity can be considerably less than that for suspensions of solid spheres. The viscosity of dilute emulsions is then described by the *Taylor equation*:[12]

$$\frac{\mu_{\text{eff}}}{\mu_0} = 1 + \left(\frac{\mu_0 + \frac{5}{2}\mu_1}{\mu_0 + \mu_1}\right)\phi \tag{1.6-5}$$

in which μ_1 is the viscosity of the disperse phase. It should, however, be noted that surface-active contaminants, frequently present even in carefully purified liquids, can effectively stop the internal circulation;[13] the droplets then behave as rigid spheres.

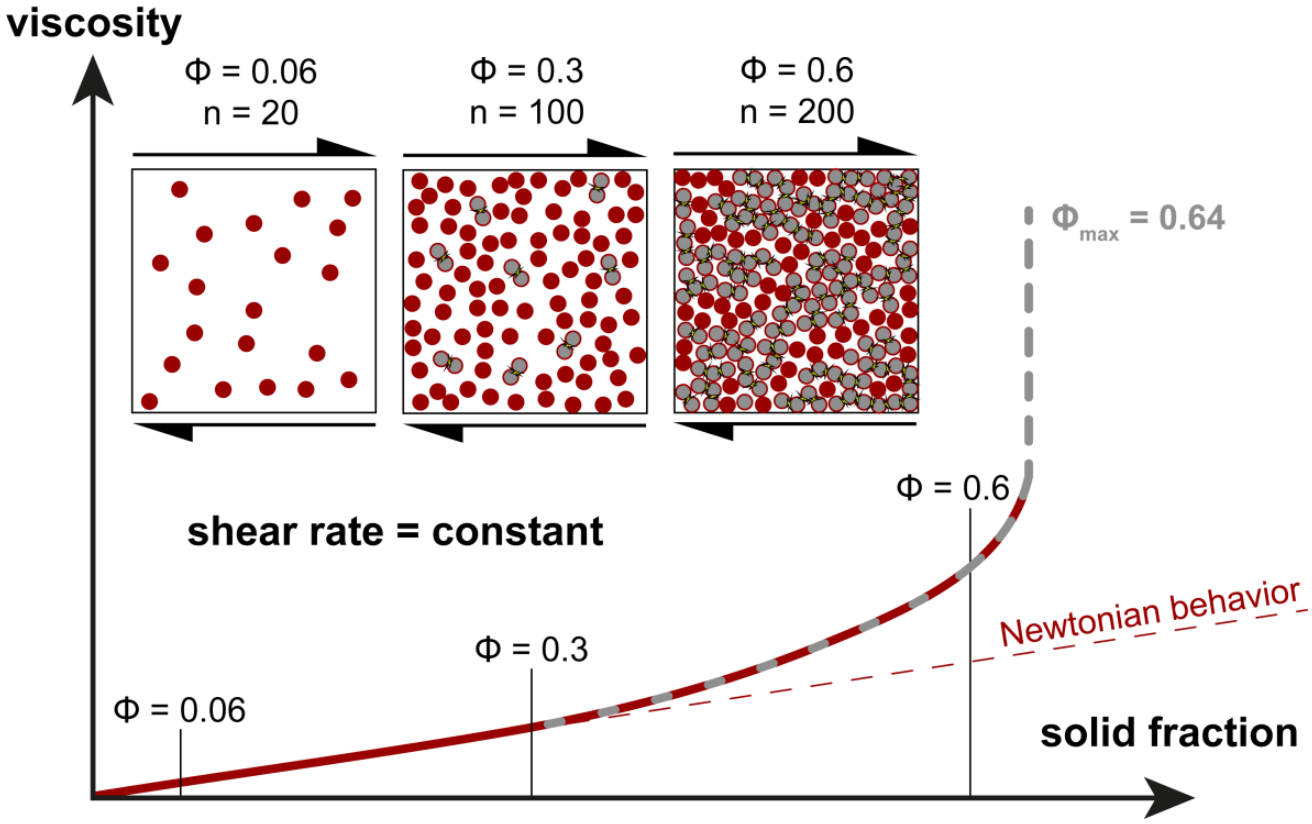
For *dilute suspensions of charged spheres*, Eq. 1.6-1 may be replaced by the *Smoluchowski equation*[14]

$$\frac{\mu_{\text{eff}}}{\mu_0} = 1 + \frac{5}{2}\phi\left(1 + \frac{(D\zeta/2\pi R)^2}{\mu_0 k_e}\right) \tag{1.6-6}$$

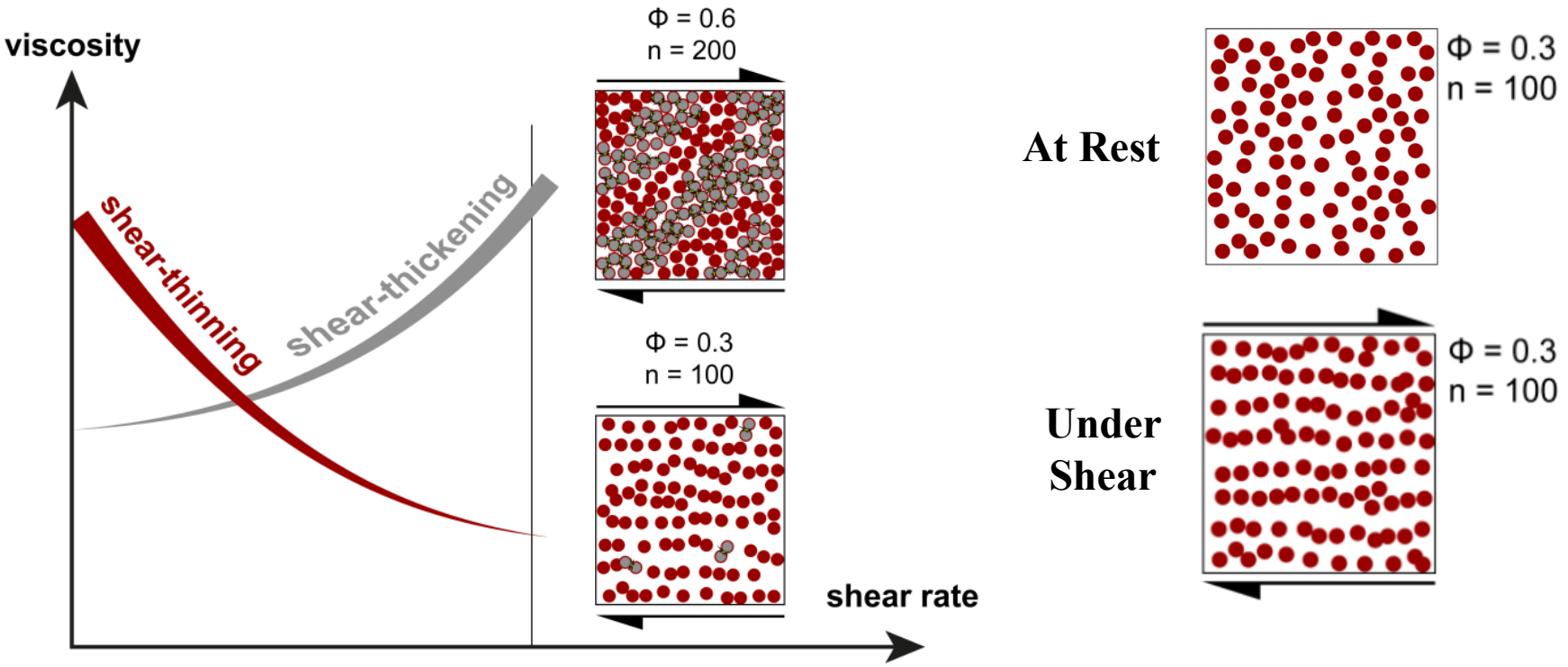
in which D is the dielectric constant of the suspending fluid, k_e the specific electrical conductivity of the suspension, ζ the electrokinetic potential of the particles, and R the particle radius. Surface charges are not uncommon in stable suspensions. Other, less well understood, surface forces are also important and frequently cause the particles to form loose aggregates.[4] Here again, non-Newtonian behavior is encountered.[15]

Viscosity of Non-Newtonian Solutions

Non-Newtonian behavior is observed for concentrated suspensions, even when the suspended particles are spherical.[11] This means that the viscosity depends on the velocity gradient and may be different in a shear than it is in an elongational flow. Therefore, equations such as Eq. 1.6-2 must be used with some caution.

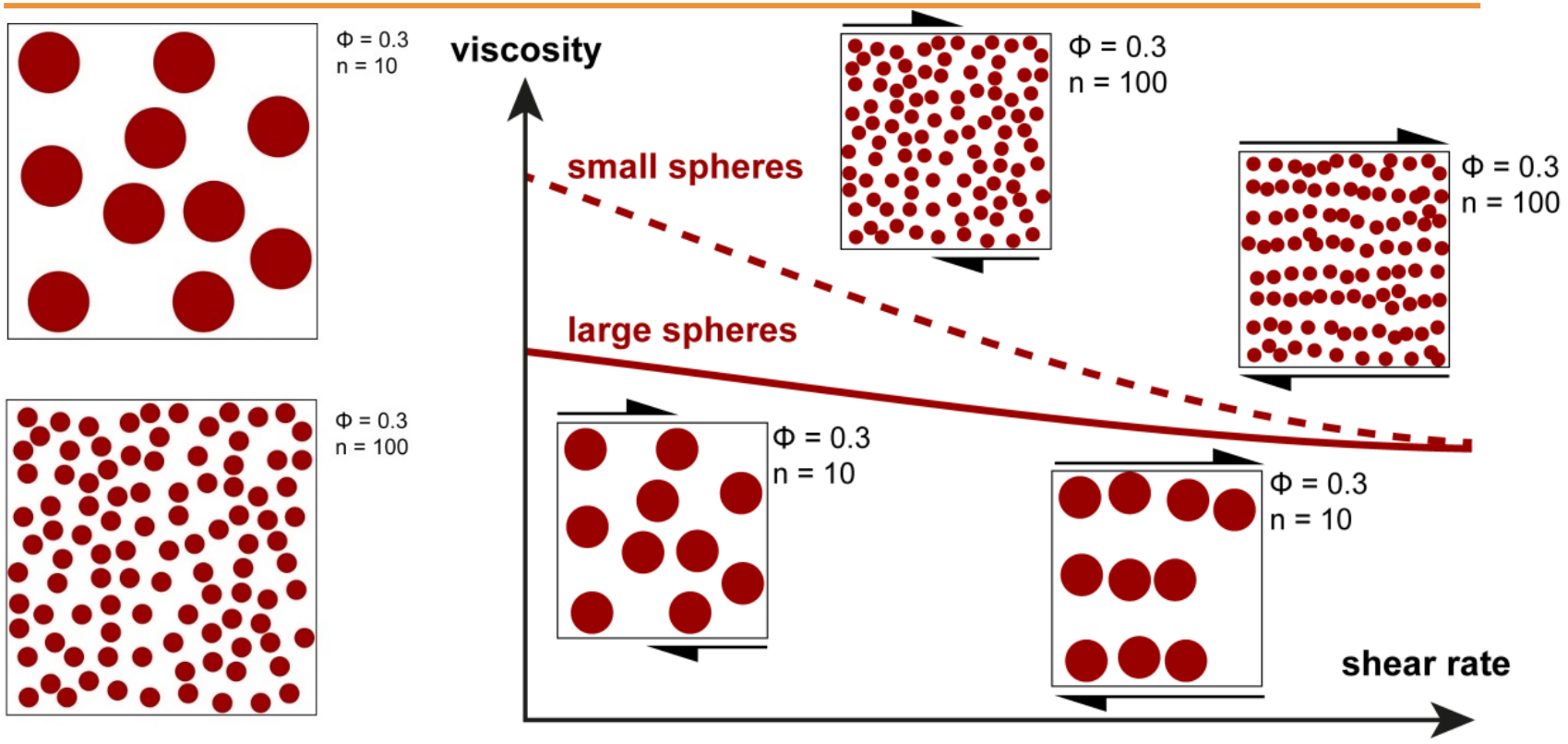


Viscosity of Non-Newtonian Solutions



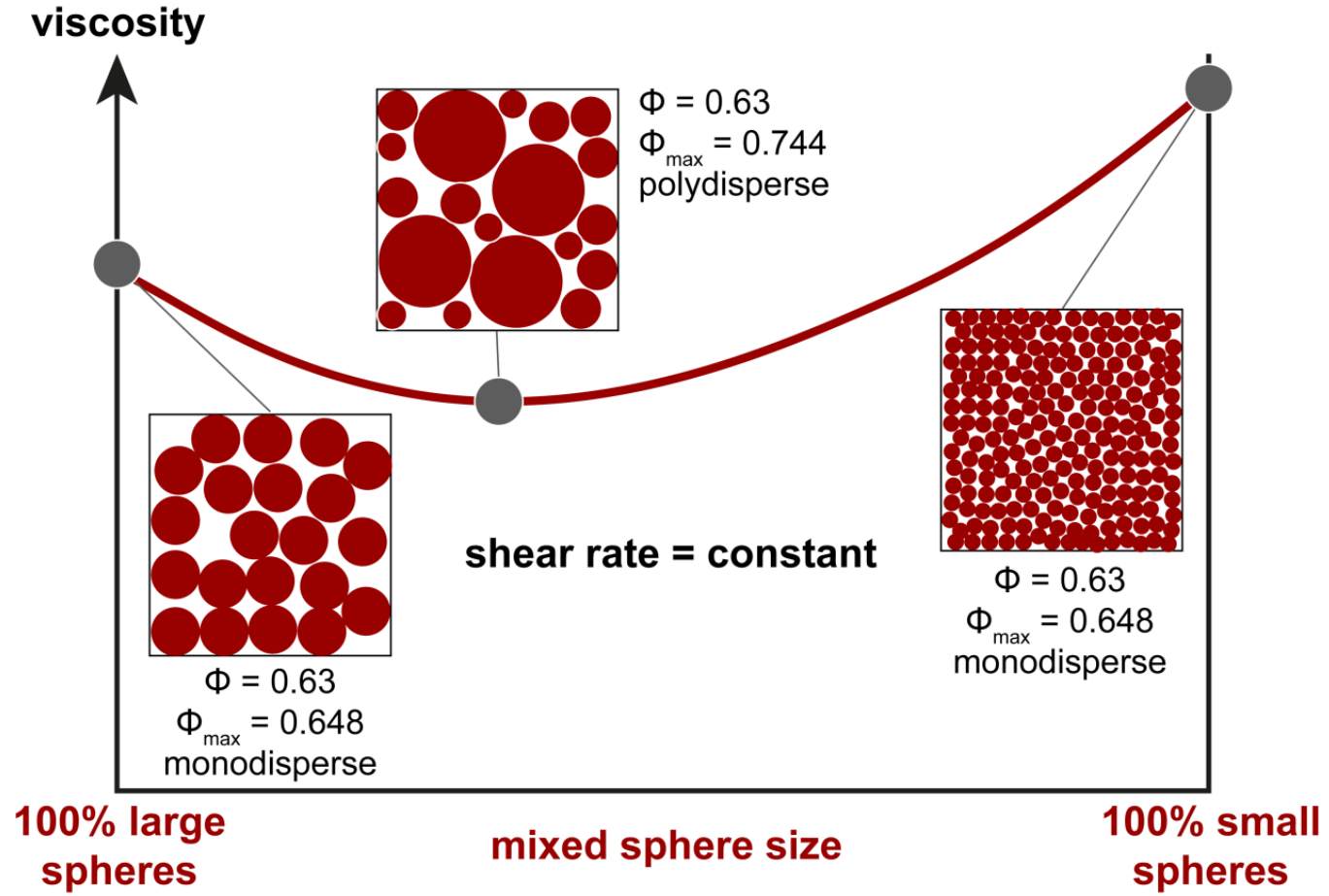
At a certain value of solid fraction, when particle-particle interaction becomes significant, shear-thinning behavior is observed. Due to alignment of particles in direction of streamlines, the molecular interaction is decreased and flow shows the shear-thinning behavior. In addition, at higher shear rates particles form clusters and jamming occurs, leading to shear. The transition from shear-thinning to shear-thickening is sample-specific and controlled by factors like particle size (distribution) and particle shape.

Viscosity of Non-Newtonian Solutions: Effect of Particle Size



For a given solid fraction, smaller particle size leads to a higher number of particles in a given volume. Therefore, the particle surface area can be several orders of magnitude higher for smaller particles. Very small particles display Brownian motion acting against an applied shear force. Therefore, surface charge, adsorption, and hydration have a potentially strong effect on the effective hydrodynamic particle size for small particles in particular.

Viscosity of Non-Newtonian Solutions: Polydisperse VS Monodisperse



Polydisperse suspensions have a higher φ_{max}. For a constant solid fraction (here: 0.63), φ/φ_{max} decreases and results in a viscosity minimum for such polydisperse suspensions.

Viscosity of Non-Newtonian Solutions: Intrinsic Viscosity and Inherent Viscosity

Obviously, particles often display uneven convexity or non-spherical shape (elongation). The intrinsic viscosity [η] is a factor to describe the particle shape. It is defined as:

$$[\eta] = \lim_{\phi \to 0} \frac{\eta - \eta_0}{\eta_0 \phi}$$

where η is viscosity of suspension, η_0 is the viscosity at zero shear rate and φ is volume fraction. When the solute particles are rigid spheres at infinite dilution, the intrinsic viscosity equals to 2.5. Therefore, the difference of intrinsic viscosity of any suspension from 2.5 shows the level of deviation of solute particles from spherical shape. According to the above equation, the intrinsic viscosity [η] is dimensionless.

Note:

The intrinsic viscosity should not be confused with inherent viscosity (η_{inh}), which is the ratio of the natural logarithm of the relative viscosity to the mass concentration of the polymer.

$$\eta_{inh} = \frac{\ln \eta_{rel}}{c} \qquad \eta_{rel} = \frac{\eta}{\eta_s}$$

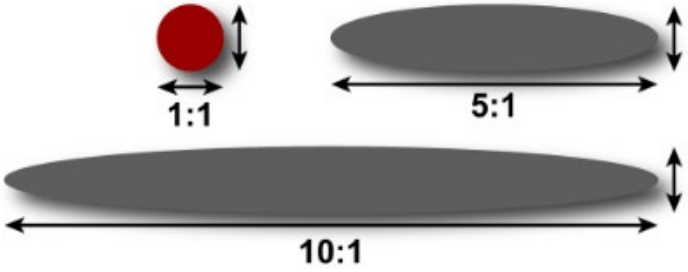
where η_{rel} is relative viscosity, c is mass concentration (g/dL), η is viscosity and η_s is viscosity of the solvent. The unit of inherent viscosity is dL/g.

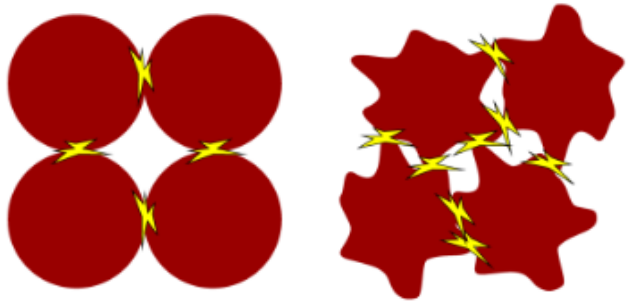
Viscosity of Non-Newtonian Solutions: The Effect of Particle Shape

As mentioned before, the intrinsic viscosity $[\eta]$ shows the shape of particles. For example, spheres are represented by a value of 2.5 and ellipsoids with a 5:1, 10:1, 50:1 aspect ratio by values of 2.94, 3.43, 7.00. For aspect ratios (R) from 1:1 to 20:1, the intrinsic viscosity can be expressed with the following function:

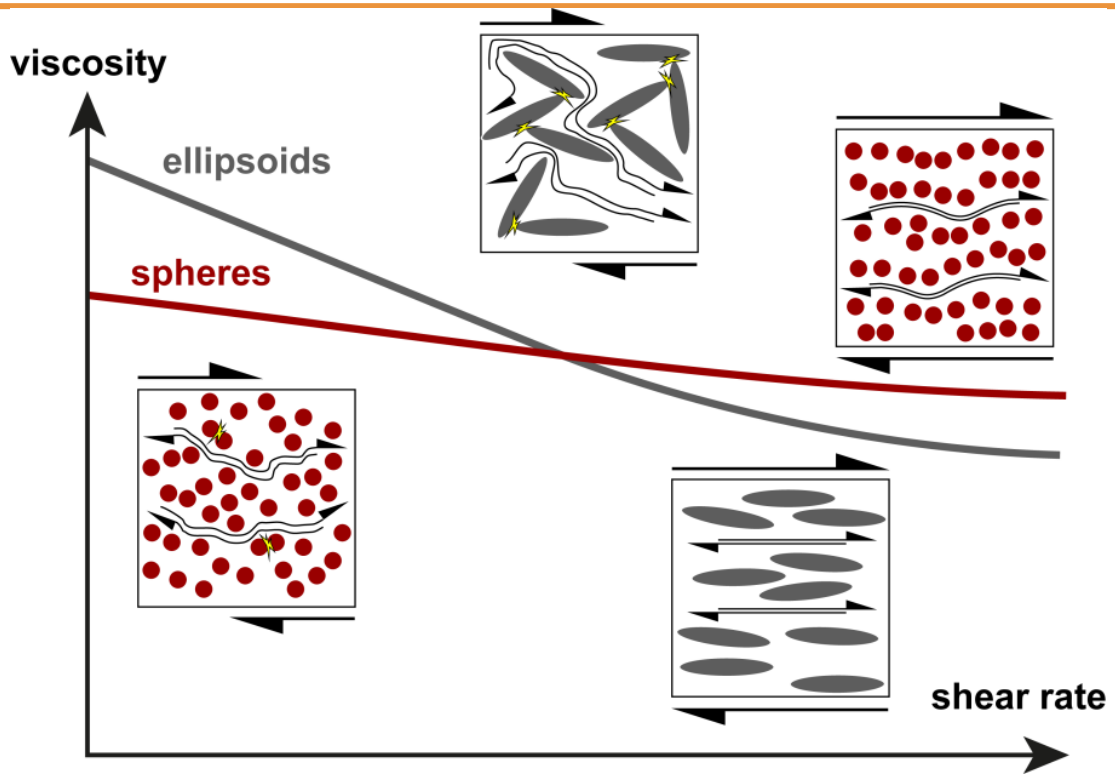
$$[\eta] = 2.5 + 0.123(R-1)^{0.925}$$

Irregularities of the particle surface lead to a higher viscosity for two reasons: The deflection of the flow lines of the solvent flowing around particles is stronger than for same-size spheres, and the increased specific particle surface increases the probability of particle-particle interactions. The effect is stronger for high particle concentrations and high shear rates.



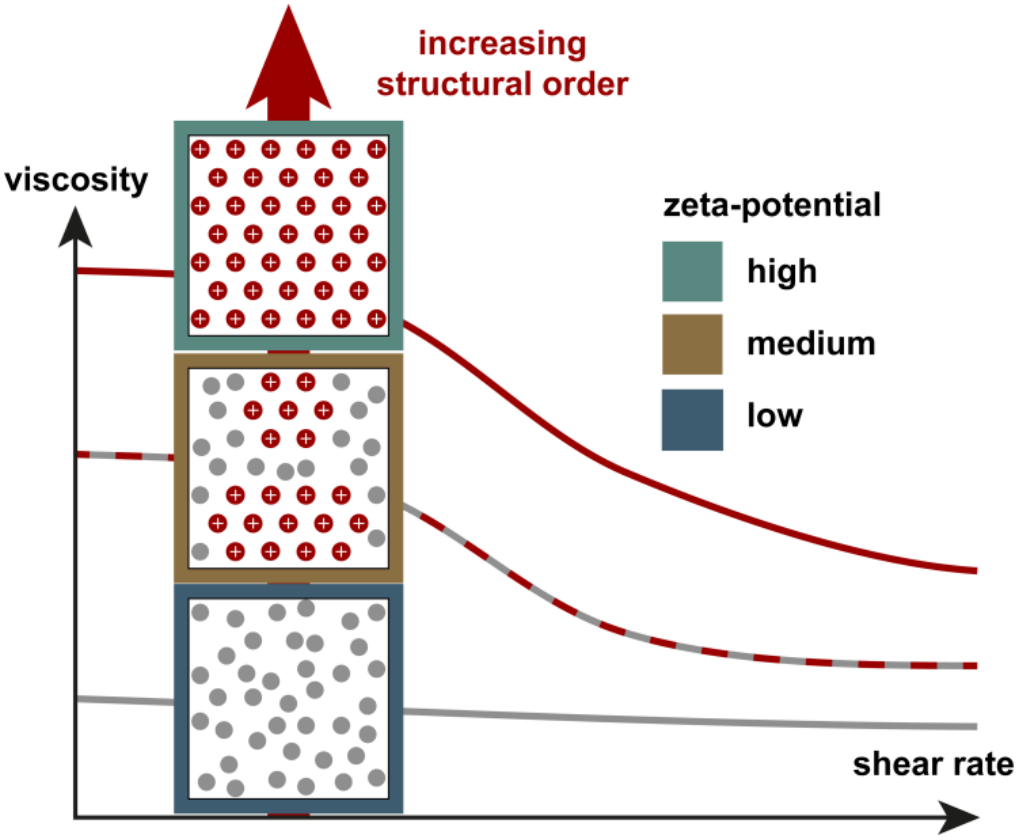


Viscosity of Non-Newtonian Solutions: The Effect of Particle Shape



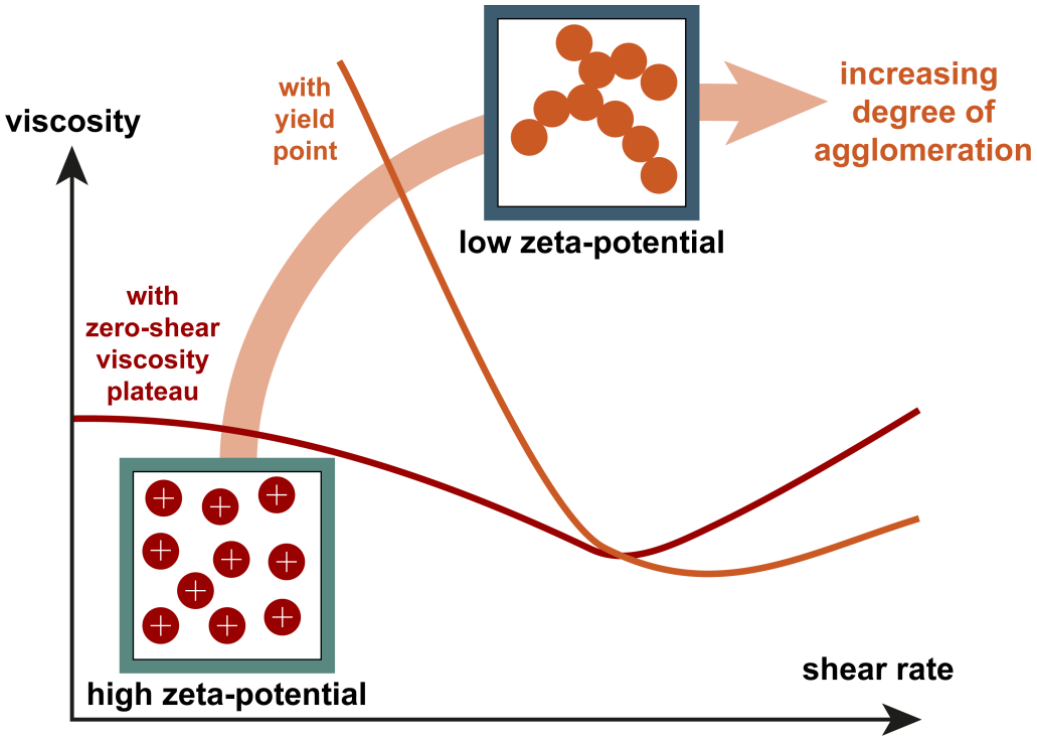
The increased surface of elongated particles leads to higher low-shear viscosity compared to spheres. However, non-spherical particles have the possibility to adapt their orientation to a flow direction. At rest, they are randomly oriented but align to the flow direction when a shear rate is applied. This leads to lower viscosity compared to spheres at higher shear rates because the intrinsic viscosity is then lower – resulting from the higher maximum packing density φ_{max} .

Viscosity of Non-Newtonian Solutions: The Effect of Electrical Charge of Small Particles



Dispersions with small particles (<1 µm) are particularly sensitive to changes in zeta potential as induced particle repulsion and increased hydrodynamic volume will increase the viscosity, in particular at low shear rates. This is only possible as gravitational forces act subordinate to such small and light particles, while Brownian motion will dominate.

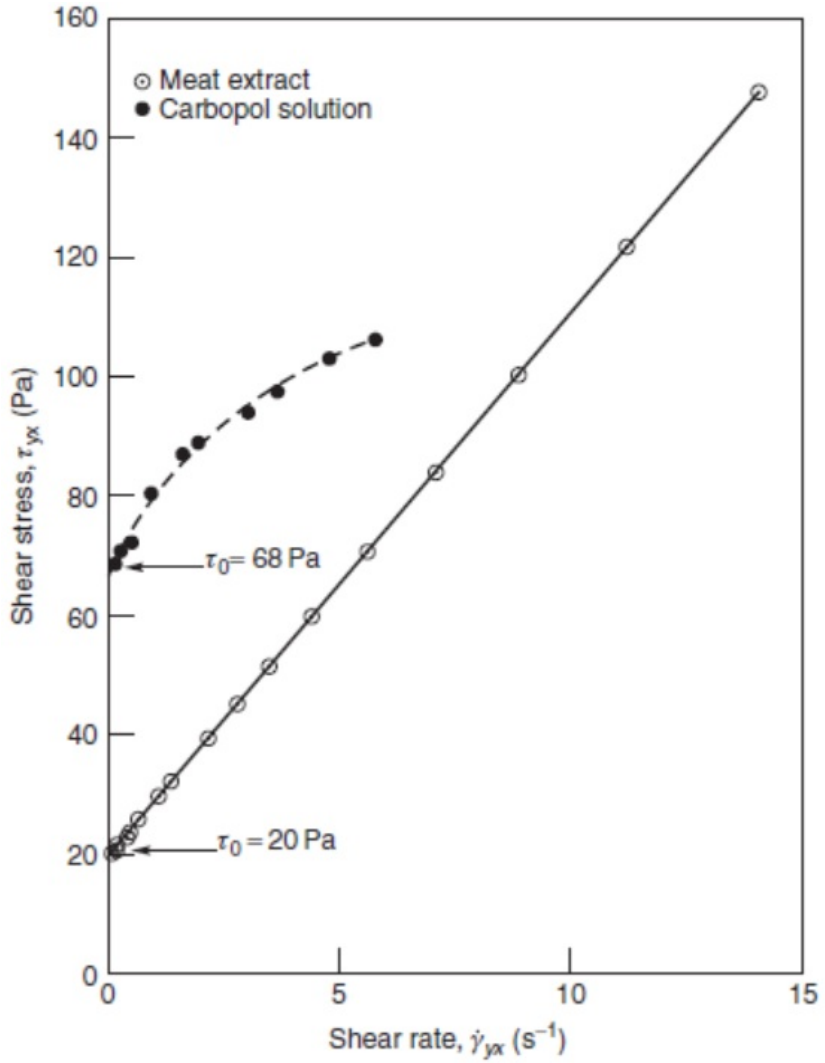
Viscosity of Non-Newtonian Solutions: The Effect of Electrical Charge of Large Particles



For large particles, at a low zeta potential, particles stick together and by steadily increasing the size of the agglomerate, gravitation will finally cause sedimentation. Such agglomeration may induce a yield point if the solid fraction is sufficiently high and the particles are able to form a three-dimensional network. Note the contrasting behavior at high shear rates, where shear thickening may occur, as inter-particle repulsion causes higher viscosities for samples with a high zeta potential.

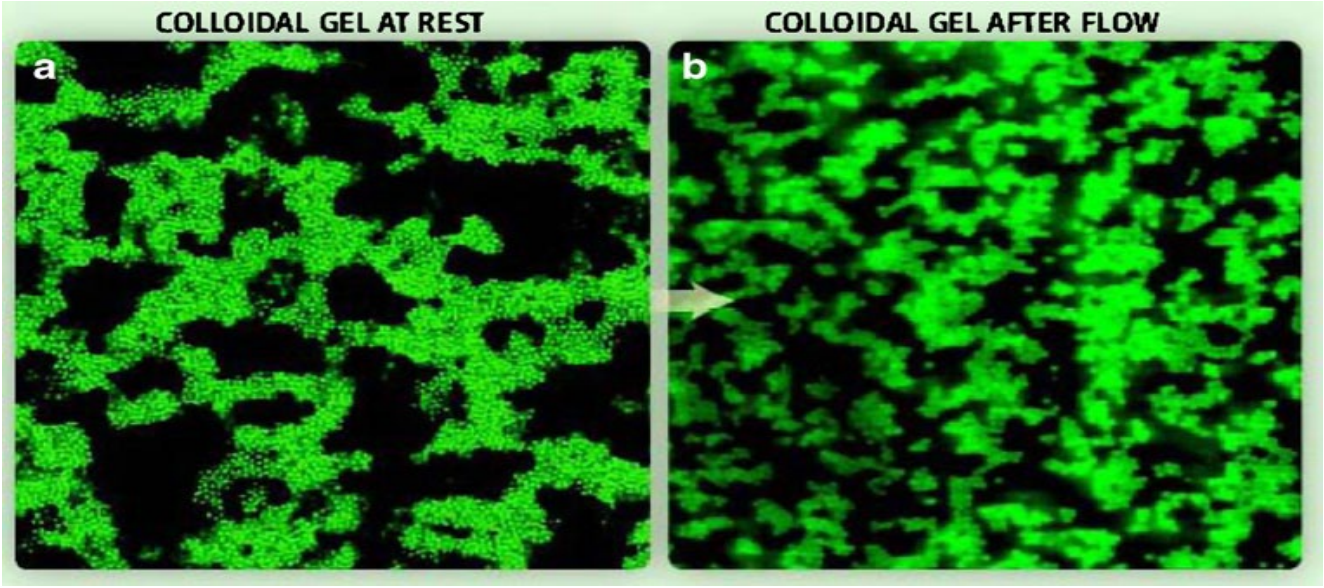
Viscoplastic Fluids

This type of fluid behavior is characterized by the existence of a yield stress (τ_0) which must be exceeded before the fluid will deform or flow.



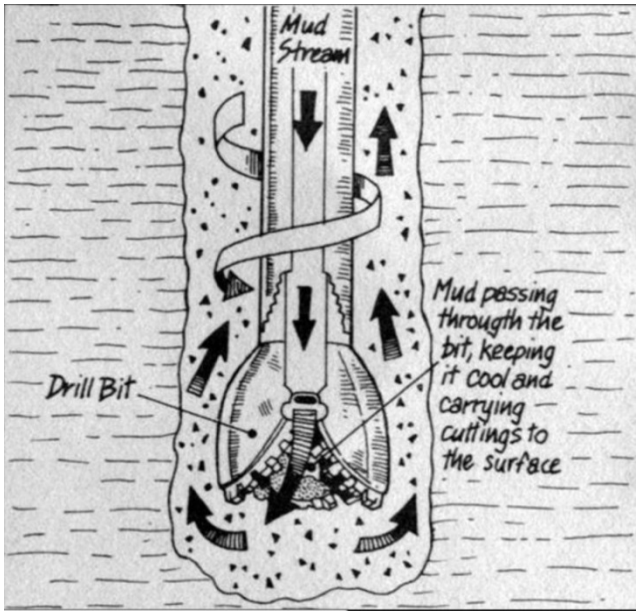
Origin of Viscoplasticity

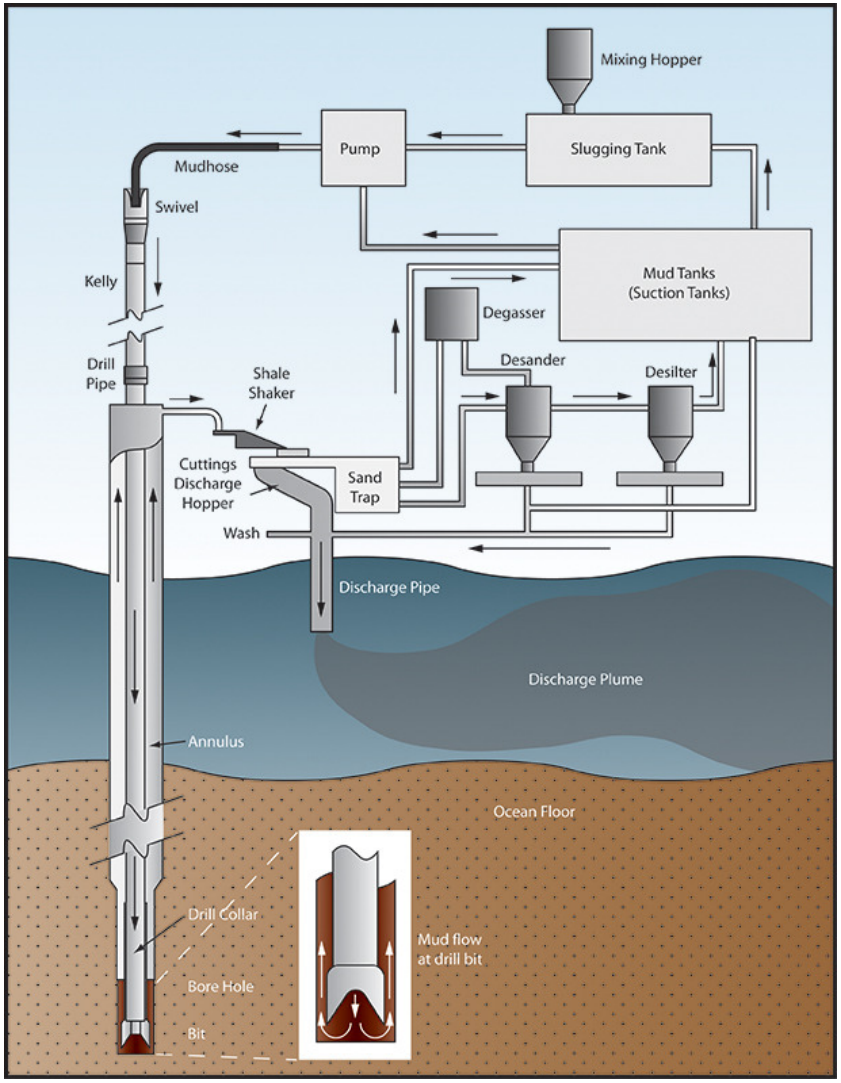
At rest, these fluids contain stress-dependent microstructures. The equilibrium structure determines an equilibrium yield stress. As the flow begins, the structure breaks down; the new structure will have a smaller yield stress and more mobility. This is a positive feedback system, and it may run away.



A colloidal gel (**a**) at rest, with a percolated structure and a yield stress of ~5 Pa, and (**b**) just after flow.

Viscoplastic Fluids: Drilling Mud





Viscoplastic Fluids: Modeling

Bingham Plastics:

$$\begin{cases} |\tau_{xy}| = \tau_0 + \eta_B |\dot{\gamma}_{xy}| & \text{for} \quad |\tau_{xy}| > \tau_0 \\ \dot{\gamma}_{xy} = 0 & \text{for} \quad |\tau_{xy}| \le \tau_0 \end{cases}$$

Herschel-Bulkley Fluid:

$$\begin{cases} |\tau_{xy}| = \tau_0 + K_{HB} |\dot{\gamma}_{xy}|^n & \text{for} \quad |\tau_{xy}| > \tau_0 \\ \dot{\gamma}_{xy} = 0 & \text{for} \quad |\tau_{xy}| \le \tau_0 \end{cases}$$

Casson Fluid Model:

$$\begin{cases} |\tau_{xy}|^{1/2} = \tau_0^{1/2} + \left(\eta_C |\dot{\gamma}_{xy}|\right)^{1/2} & \text{for} \quad |\tau_{xy}| > \tau_0 \\ \dot{\gamma}_{xy} = 0 & \text{for} \quad |\tau_{xy}| \le \tau_0 \end{cases}$$

- Many foodstuffs and biological materials, especially blood, are well described by Casson Model.

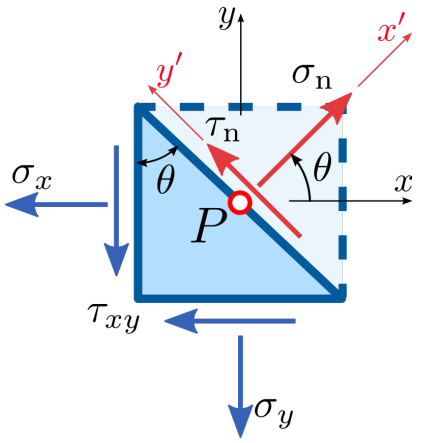
Viscoplastic Fluids: Modeling of Complex Flows

• For complex flows, we should use the von-Mises yield criterion to define the condition in which the shear flow is occurred:

$$\sqrt{\frac{1}{2}II_\tau} > \tau_0$$

where

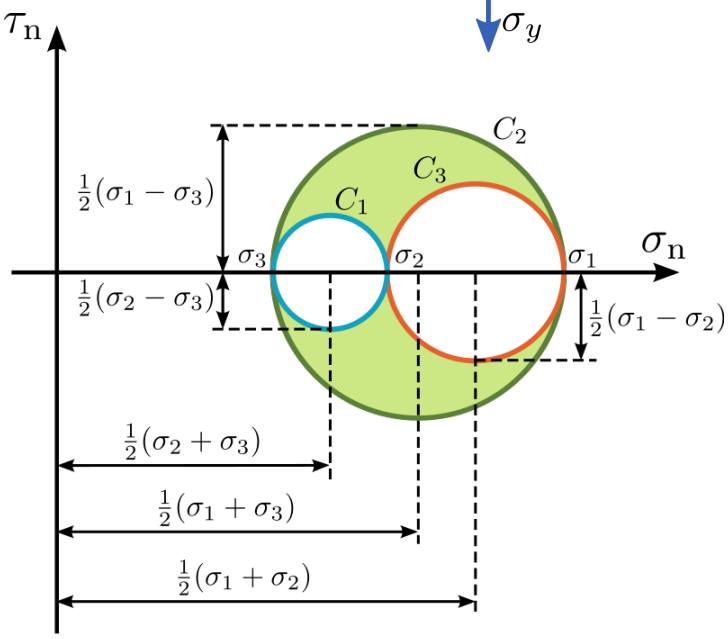
$$II_\tau = tr(\boldsymbol{\tau}^2)$$



• For example, using the von-Mises yield criterion, the equation of Bingham plastic is:

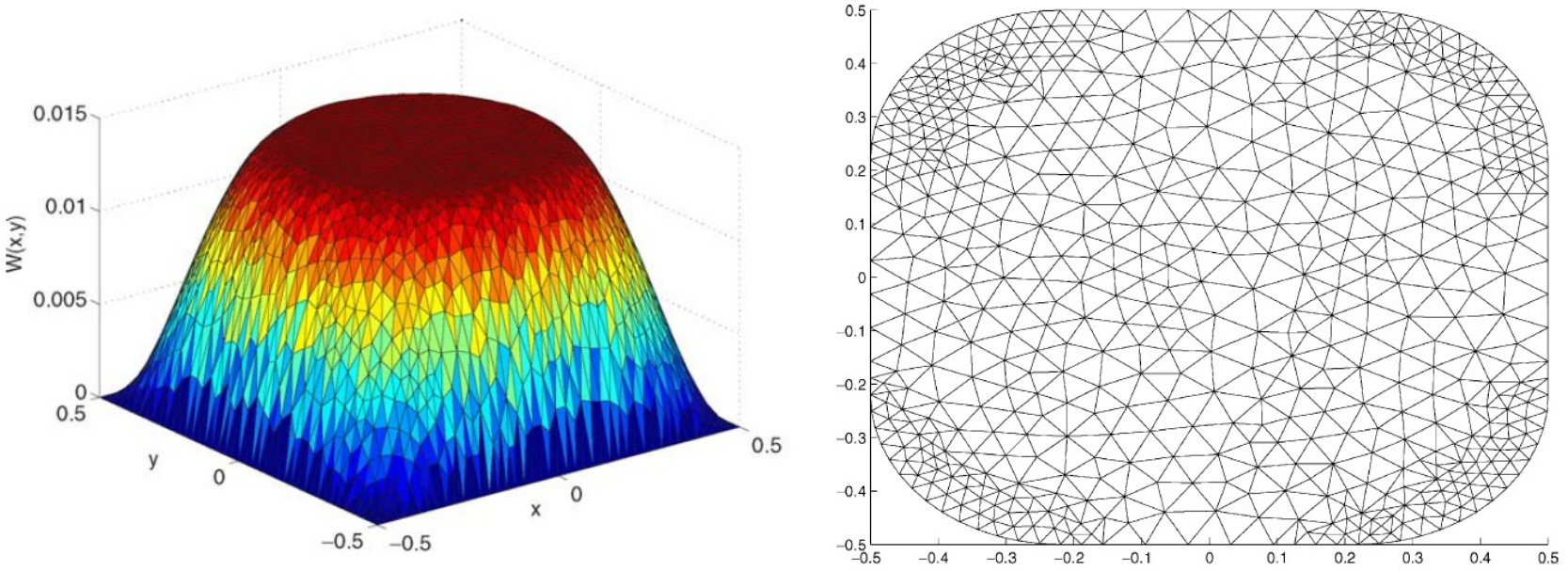
$$\begin{cases} \boldsymbol{\tau} = \left(\dfrac{\tau_0}{q} + \eta\right)\dot{\boldsymbol{\gamma}} & \sqrt{\dfrac{1}{2}II_\tau} > \tau_0 \\ \dot{\boldsymbol{\gamma}} = 0 & \sqrt{\dfrac{1}{2}II_\tau} \le \tau_0 \end{cases}$$

where q is the generalized shear rate.



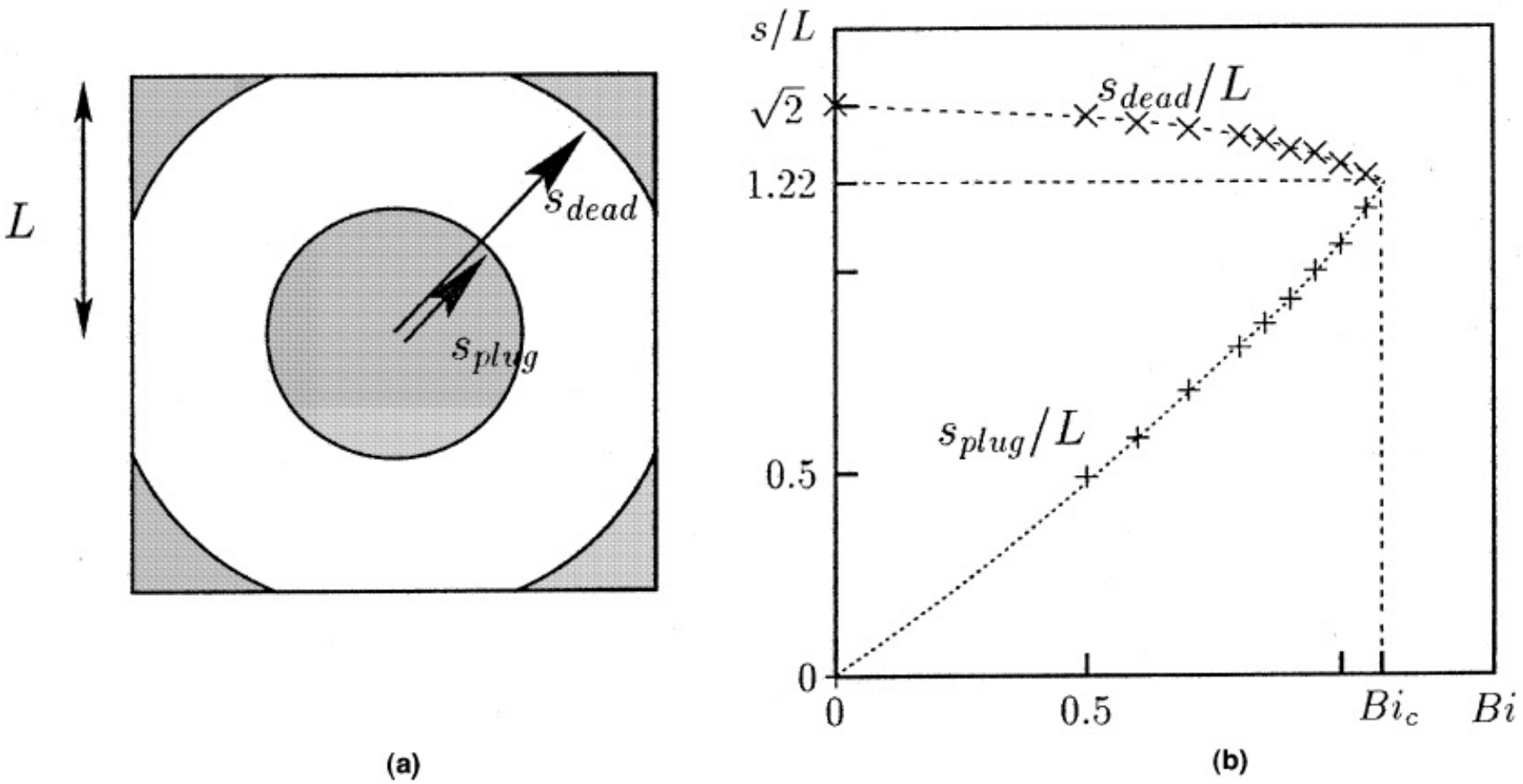
Viscoplastic Fluids: Modeling of Complex Flows

The main challenge to model 3D flows of viscoplastic fluids is determining the interface between yielded and un-yielded regions.



Flow of Bingham plastic inside a straight rectangular duct at Bi=0.8

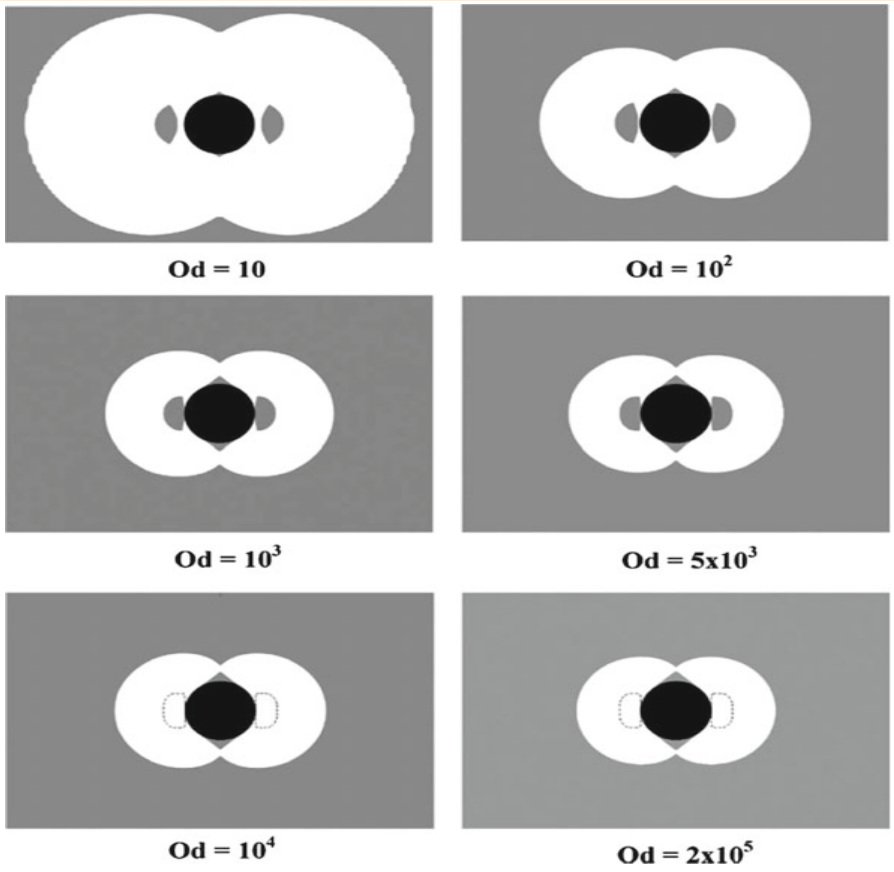
Viscoplastic Fluids: Modeling of Complex Flows



Intersection of the yield surface with the diagonal: (a) schematics and notations; (b) computations and extrapolation.

Viscoplastic Fluids: Modeling of Complex Flows

Limiting flow around a circular cylinder.



For more information about this issue, refer to:
Frigaard I.A. (2019) Background Lectures on Ideal Visco-Plastic Fluid Flows. In: Ovarlez G., Hormozi S. (eds) Lectures on Visco-Plastic Fluid Mechanics. CISM International Centre for Mechanical Sciences (Courses and Lectures), vol 583. Springer, Cham

Viscoplastic Fluids: Modeling of Complex Flows, Principles For Correct Velocity and Stress Fields

Minimum principle

Among all velocity fields with piecewise-continuous first derivatives which satisfy the equation of continuity and the boundary conditions on S_V, the solution to the Bingham-flow equation minimizes the dimensional expression

$$H^* = \int_V (\eta_0 \dot{\gamma}^{*2} + 2\tau_y \dot{\gamma}^*)\, \mathrm{d}V. \tag{2.15}$$

Maximum principle

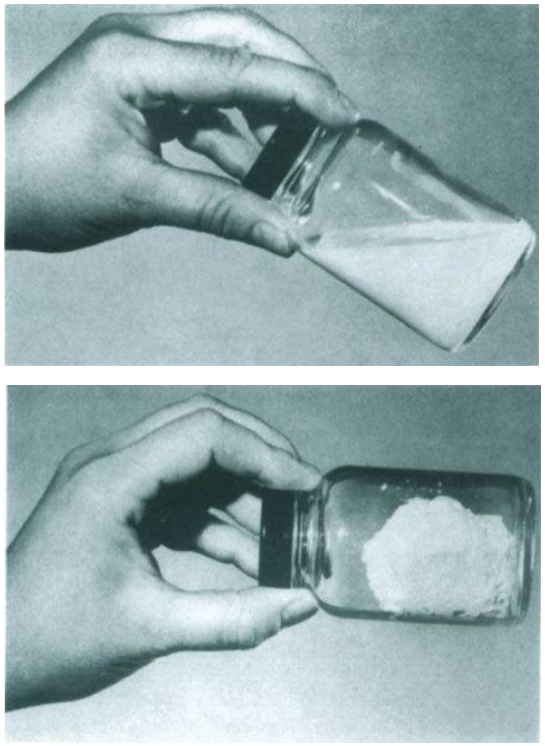
Among all stress fields with piecewise-continuous first derivatives that satisfy the equations of motion, the actual stress field $\boldsymbol{\tau}^*$ maximizes the expression

$$K^* = -\frac{1}{4}\int_V [\,|\tau^* - \tau_y| + \tau^* - \tau_y]^2\, \mathrm{d}V + 2\int_{S_V} \boldsymbol{n}\cdot[\boldsymbol{\tau}^*\cdot\boldsymbol{v}^*]\, \mathrm{d}S. \tag{2.16}$$

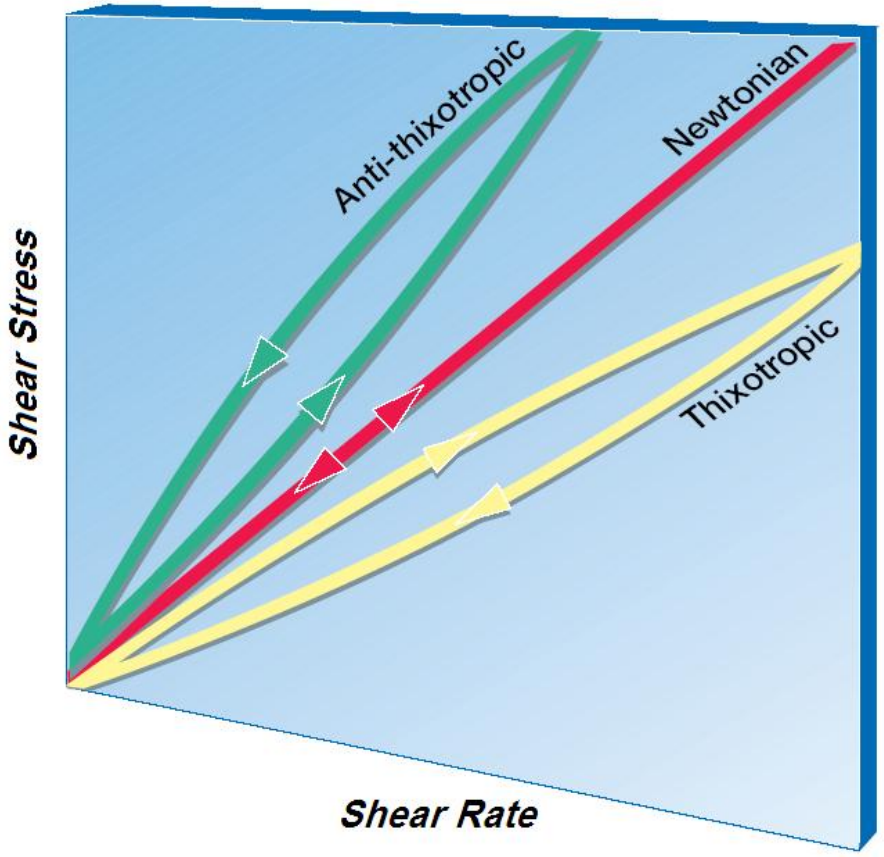
Both expressions (2.15) and (2.16) take the same limiting value when evaluated with the velocity and stress fields that satisfy the Bingham-plastic constitutive equation. We use the calculation of H^* and K^* as a test of accuracy for our numerical algorithm.

Time-Dependent Fluids

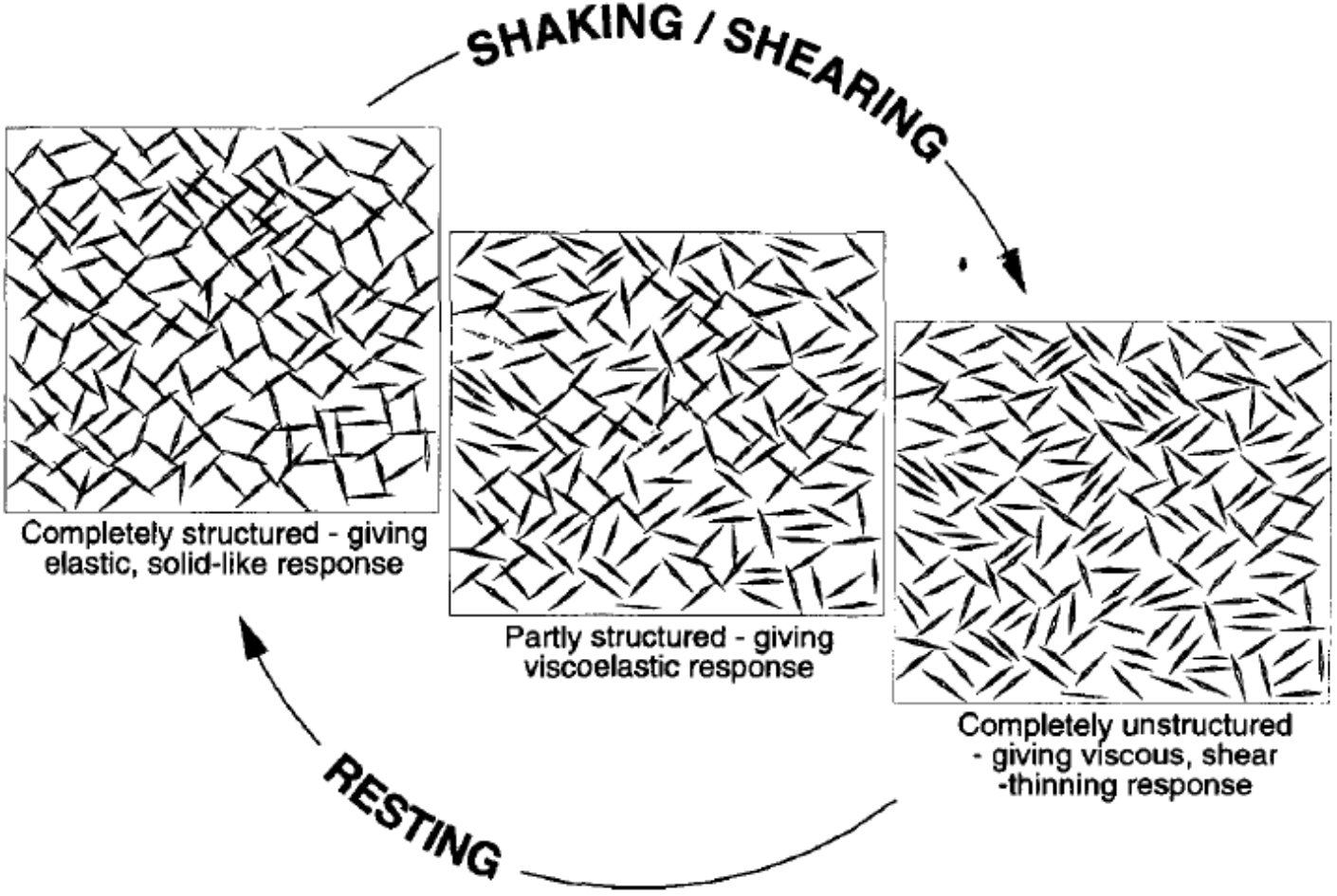
In practice, apparent viscosities may depend not only on the rate of shear but also on the time for which the fluid has been subjected to shearing.



A liquid (an alkaline perbunan latex) which shows the anti-thixotropic behavior.

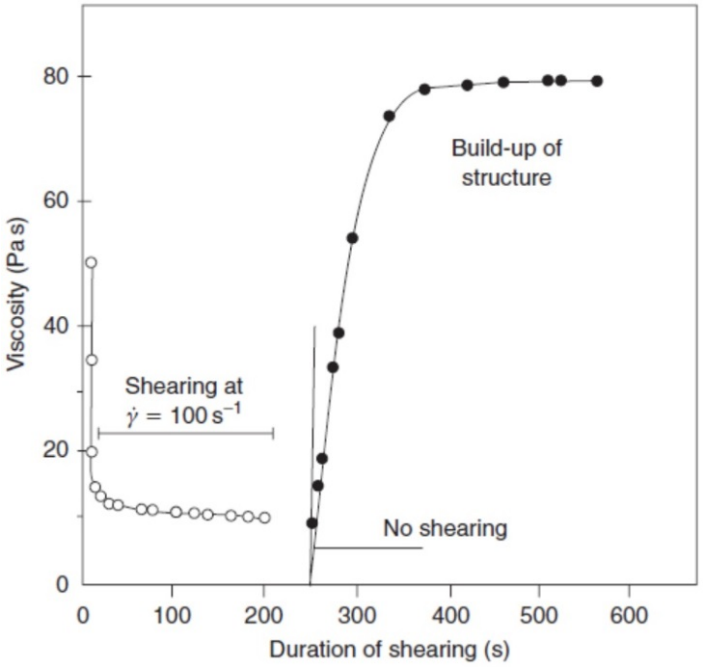


Time-Dependent Fluids

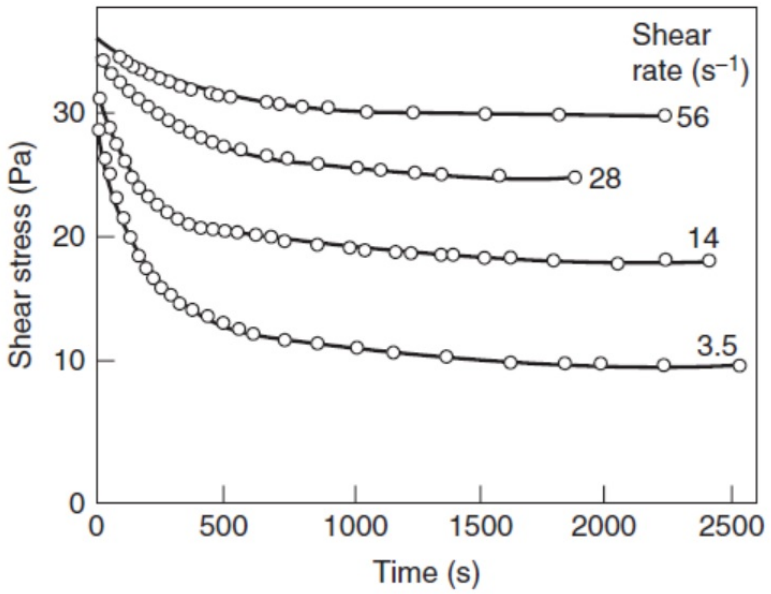


Breakdown of a 3D thixotropic structure.

Time-Dependent Fluids



Breakdown and re-formation of structure in a proprietary body lotion.



Representative data showing thixotropy in a 59% (by weight) red mud suspension.

The thixotropic behavior is observed in bentonite–water suspensions, red mud suspensions (waste stream from aluminum industry), metal slushes, cement paste, crude oils and certain foodstuffs, some inks and coatings, some detergent systems.

The rheopectic behavior is reported to occur with suspensions of ammonium oleate, aqueous gypsum paste, some colloidal suspensions of vanadium pentoxide at moderate shear rates, coal–water slurries and protein solutions.

Time-Dependent Fluids: Modeling

There are some formulations for viscosity of thixotropic fluids which have been derived based on the some different theories. For example, the following equation has been expressed based on an indirect microstructural theory:

$$\eta(\sigma, t) = \eta(\lambda) = \frac{\eta_\infty}{(1 - K\lambda)^2}, \quad K = 1 - \left(\frac{\eta_\infty}{\eta_0}\right)^{1/2},$$

$$\frac{d\lambda}{dt} = g(\dot{\gamma}, \lambda) = a(1 - \lambda)^b - c\lambda\dot{\gamma}^d,$$

where a, b, c and d are constants for any one system. If the value of g is negative, the system is breaking down towards equilibrium; if it is positive, it is building up towards equilibrium. At equilibrium, for every value of shear rate, there is a particular value of λ which in this equation is found by setting dλ /dt to zero.

For more information about the other formulations, refer to:

H. A. Barnes, Thixotropy-A Review, Journal of non-Newtonian Fluid Mechanics, 70 (1991), 1-33.


Thanks!