1. Introduction
Multiphase materials occur in many fields of natural and engineering science, industry, and daily life. Biological materials such as blood or cell suspensions, pharmaceutical or food products, inorganic materials such as concrete, drilling mud, printing inks, and multicomponent metal melts.

2. Single Particulate Systems

2.1. Introduction
In many practical applications, we need to know the force required to move a solid object through a surrounding fluid, or conversely, the force that a moving fluid exerts on a solid as the fluid flows past it. The liquid phase may exhibit complex non-Newtonian behavior. It is often necessary to calculate the fluid dynamic drag on solid particles. The need to estimate the terminal falling (or rising) velocity of a solid (or fluid) particle arises frequently in process engineering and design calculations. Experience with Newtonian fluids has shown that the hydrodynamics of systems consisting of single particles serves as a useful starting point for understanding the mechanics of the more complex multi-particle systems.

2.2. Drag on a Sphere
The total drag force:

\[ F_D = F_t + F_n \]  \hspace{1cm} (2.1)

Is often expressed using a dimensionless drag coefficient:

\[ C_D = \frac{F_D}{\left(\frac{1}{2} \rho V^2 \right)(\pi R^2)} \]  \hspace{1cm} (2.2)

2.2.1. In Power-Law Fluids
For power-law fluids, the drag coefficient can be expressed in terms of the Reynolds number and the power-law index:

\[ C_D = f(Re, n) \]  \hspace{1cm} (2.3)

For the creeping flow region (Re<<1), the numerical results may be expressed as a deviation factor X(n), in the relation between drag coefficient and Reynolds number obtained from Stokes law:

\[ C_D = \frac{24}{Re} X(n) \]  \hspace{1cm} (2.4)
Where $Re = \frac{\rho V^2 - n \cdot d^n}{m}$

The numerical values of $X(n)$ for both shear-thinning and shear-thickening fluid behavior are listed in Table 1.

Table 1. Values of $X(n)$ for a sphere

<table>
<thead>
<tr>
<th>$n$</th>
<th>$X(n)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.8</td>
<td>0.261</td>
</tr>
<tr>
<td>1.6</td>
<td>0.390</td>
</tr>
<tr>
<td>1.4</td>
<td>0.569</td>
</tr>
<tr>
<td>1.2</td>
<td>0.827</td>
</tr>
<tr>
<td>1.0</td>
<td>1.002</td>
</tr>
<tr>
<td>0.9</td>
<td>1.14</td>
</tr>
<tr>
<td>0.8</td>
<td>1.24</td>
</tr>
<tr>
<td>0.7</td>
<td>1.32</td>
</tr>
<tr>
<td>0.6</td>
<td>1.382</td>
</tr>
<tr>
<td>0.5</td>
<td>1.42</td>
</tr>
<tr>
<td>0.4</td>
<td>1.442</td>
</tr>
<tr>
<td>0.3</td>
<td>1.458</td>
</tr>
<tr>
<td>0.2</td>
<td>1.413</td>
</tr>
<tr>
<td>0.1</td>
<td>1.354</td>
</tr>
</tbody>
</table>

Shear-thinning behavior causes drag increase ($X>1$), and drag reduction ($X<1$) occurs in shear-thickening fluids. Numerical results in Table 1 are well correlated by the following analytic expression:

$$X(n) = 6^{(n-1)/2} \left[ \frac{3}{n^2 + n + 1} \right]^{n+1}$$  \hspace{1cm} (2.5)

Numerical predictions of drag on a sphere moving in a power-law fluid are available for the sphere Reynolds number up to 500, and the values of drag coefficient are best represented by the following:

$$C_D = \frac{24}{Re} \left[ 1 + 0.148 \cdot Re^{2.35(2.42n+0.918)} \right]$$  \hspace{1cm} (2.6)

The empirical constants are based on numerical results extending over the range of conditions as: $0.5 \leq n \leq 2$ and $5 \leq Re \leq 500$. Collating most of the literature data, previous work was extended to estimate drag on a sphere in power-law fluids as:

$$C_D = C_{D0} + 0.44X C_{D0}^{2A0} B_0 \left[ \frac{6X(n)b_0}{6X(n)b_0 + C_{D0}} \right]^{1/2} + 0.44 \left[ \frac{6X(n)b_0}{6X(n)b_0 + 128C_{D0}} \right]^{1/12}$$  \hspace{1cm} (2.7)

Where $C_{D0}$ is given by equation (2.4) and:
For a known value of the power-law index, the three constants $A_0$, $B_0$, and $b_0$ are known. $\chi$ is the ratio of the surface area to the projected (normal to the direction of settling) area of the particle. This equation is also successful in correlating most of the currently available drag results for non-spherical particles. For a sphere of diameter $d$, the value of the composite shape factor $\chi$ is equal to $\frac{\pi d^2}{(\pi d^2/4)}$, i.e. $\chi=4$.

### 2.2.2. In Viscoplastic Fluids

A viscoplastic material in an unsheared state will support an immersed particle for an indefinite period of time. Before undertaking an examination of the drag force on a spherical particle in a viscoplastic medium, the question of static equilibrium will be discussed and a criterion will be developed to delineate the conditions under which a sphere will either settle or be held stationary in a liquid exhibiting a yield stress.

**Static equilibrium.** A dimensionless group, $Y$, denotes the ratio of forces due to the yield stress and due to gravity:

$$Y = \frac{\tau_0}{gd(\rho_s - \rho)}$$  \hspace{1cm} (2.12)

Small values of $Y$ will favor motion of a sphere. Critical values of $Y$ reported by various investigators fall in two categories. One group, with the value of $Y$ in the range $0.06 \pm 0.02$, includes numerical predictions, observations on the motion/no motion under free fall conditions, and the residual force upon the cessation of flow. Experimental results based on the extrapolation of force-velocity data to zero velocity also yield the value in the range $0.048 \leq Y \leq 0.088$. The second group, with $Y \sim 0.2$, relies on the intuitive consideration that the buoyant weight of the sphere is supported by the vertical component of the force due to

\[
b_0 = \exp\{3(C_1 - \ln 6)\} \tag{2.8}
\]

\[
C_1 = \left\{6^{(1-n)/2} X(n)\right\}^{1/n+1} \tag{2.9}
\]

\[
B_0 = \frac{3 - C_1}{6C_1} \exp\left\{\frac{1}{2} \left(\frac{3 - C_1}{C_1}\right) \ln 3\right\} \tag{2.10}
\]

\[
A_0 = \frac{11}{48} \sqrt{6} \left[1 - \exp\left\{\frac{3 - C_1}{2C_1} \ln \frac{\sqrt{6} - 1}{\sqrt{6}}\right\}\right] \tag{2.11}
\]
the yield stress, and on measurements on a fixed sphere held in an unsheared viscoplastic material. The large discrepancy between the two sets of values suggests that there is a fundamental difference in the underlying mechanisms inherent in these two approaches.

Flow field. Figure 1 shows the typical size and shape of deformation cavity for a range of values of the sphere to tube diameter ratio and the Bingham number, $Bi(\equiv \tau_B^{B} d/V \mu_B)$.

![Figure 1. Size of sheared cavity around a sphere moving in a viscoplastic solution.](image)

Drag force. The finite element method was used to evaluate the total drag on a sphere moving slowly (creeping regime) in a Bingham plastic medium in terms of correction factor, $X(=C_D Re_B/24)$, which becomes a function of the Bingham number, $Bi(\equiv \tau_B^{B} d/V \mu_B)$, as:

$$X = 1 + a(Bi)^b$$  \hspace{1cm} (2.13)

For the case of $d/D=0$ (no wall effects), $a=2.93$ and $b=0.83$. In the range $0 \leq d/D \leq 0.5$, the values of $a$ and $b$ vary in the ranges $1.63 \leq a \leq 2.93$ and $0.83 \leq b \leq 0.95$. As the Bingham number becomes small, $X$ would be expected to approach unity. The higher drag ($X>1$) in a viscoplastic medium is attributable to the additive effects of viscosity and yield stress.

For creeping flow in a Newtonian fluid, there is a reciprocal relationship between the Reynolds number and the drag coefficient, $C_D Re=24$. For Bingham plastics this product depends on the Bingham number as seen in (2.13). The maximum value of the Reynolds number for creeping flow in a Bingham plastic is:

$$Re_{max} \approx 100Bi^{0.4}$$  \hspace{1cm} (2.14)
Thus the greater the Bingham number, the higher the Reynolds number up to which the creeping flow conditions apply for spheres moving in Bingham plastic fluids. The three parameter Herschel-Bulkley fluid model gives a somewhat better fit of the fluid rheology than the Bingham model. Correlation for drag on spheres in Herschel-Bulkley model liquids is:

\[ C_D = \frac{24}{Re} (1 + B_i^*) \]  

(2.15)

Where Reynolds number, \( Re = \frac{\rho V^{2-n} d^n}{m} \) and modified Bingham number, \( B_i^* = \frac{\tau_0^H / m (V/d)^n}{(\rho V^{2-n} d^n/m)(1 + B_i^*)} \). Equation (2.15) covers the ranges: \( 10^{-5} \leq Re \leq 0.36, 0.25 \leq B_i^* \leq 280 \), and \( 0.43 \leq n \leq 0.84 \).

Non-Newtonian characteristics seem to be much more important at low Reynolds numbers and their role progressively diminishes as the inertial effects become significant at high Reynolds number. In creeping flow, equations (2.4), (2.13), (2.15) should be used to estimate drag forces on spheres moving in power-law, Bingham model, or Herschel-Bulkley fluids. At high Reynolds numbers, the application of the standard drag curve for Newtonian fluids yields values on drag on spheres which are about as accurate as the empirical correlations available in the literature. The Reynolds number defined as \( \rho V^{2-n} d^n/m \) for power-law fluids, as \( \rho V d/\mu_B \) for Bingham plastics, and as \( (\rho V^{2-n} d^n/m)/(1 + B_i^*) \) for Herschel-Bulkley model fluids must be used in the standard Newtonian drag curve.

### 2.2.3. In Viscoelastic Fluids

Early studies suggested a slight reduction (~5-10%) in drag below the Stokes value, with the amount of drag reduction showing a weak dependence on Deborah or Weissenberg number. Subsequent simulations suggest that after an initial period of reduction, the drag on a sphere in a visco-elastic medium can exceed that in a Newtonian medium at high values of Deborah number, attributed to extensional effects in the fluid. Both drag reduction (up to 25%) and drag enhancement (up to 200%) compared with the Newtonian value have been observed experimentally. There is very little quantitative agreement among various studies. It is not yet possible to interpret and/or correlate experimental results of drag in viscoelastic fluids in terms of measurable rheological properties.
2.3. Terminal Velocity

For gravity settling of a sphere at its terminal velocity the drag force on it is equal to the buoyant weight:

\[ F_D = \frac{\pi d^3}{6} (\rho_s - \rho)g \]

(2.16)

Combining (2.16) with (2.4), the terminal velocity of a sphere in a power-law fluid is given as (Re<1):

\[ V = \left[ \frac{gd^{n+1}(\rho_s - \rho)}{18mX(n)} \right]^{1/n} \]

(2.17)

In shear-thinning power-law fluids, the terminal falling velocity shows a stronger dependence on sphere diameter and density difference than Newtonian fluid.

It is better to work in a set of new dimensionless groups which are formed by simply combining the Reynolds number, drag coefficient, and power law index. Dimensionless sphere diameter \(d^*\) and terminal falling velocity \(V^*\) in power law fluids are:

\[ d^* = \left( \frac{3}{4} C_D Re^{2/(2-n)} \right)^{(2-n)/(2+n)} \]

(2.18)

\[ V^* = \left( \frac{Re}{\left\{ (3/4) C_D \right\}^n} \right)^{1/(2+n)} \]

(2.19)

For a sphere falling under the influence of gravity, the drag coefficient is:

\[ C_D = \frac{4}{3} \frac{gd}{V^2} \left( \frac{\rho_s - \rho}{\rho} \right) \]

(2.20)

Substituting for \(C_D\) from equation (2.20) and for \(Re = (\rho V^{2-n} d^n)/m\) into (2.18) and (2.19):

\[ d^* = d \left( \frac{g(\rho_s - \rho)}{\rho} \right)^{(2-n)/(2+n)} \left( \frac{\rho}{m} \right)^{2/(2+n)} \]

(2.21)
The relationship between $d^*$ and $V^*$ is:

\[
V^* = V \left( \frac{\rho^{n+1}}{g^n m(\rho_s - \rho)^n} \right)^{1/(2+n)}
\]  

(2.22)

A value of $K_2 = 0.793$ is recommended.

2.4. Effect of Shape on Terminal Velocity and Drag Force

The most commonly used measure of the size of a non-spherical particle is the diameter of an equal volume sphere, $d_s$. The shape of a non-spherical particle is its sphericity, $\psi$. The sphericity is defined as the ratio of the surface area of the equal volume sphere to surface area of the actual particle. Since for a fixed volume, a sphere has the minimum surface area, the sphericity is always less than unity. Smaller values of $\psi$ represent larger deviation from the spherical. The equal volume sphere diameter and the sphericity are fixed for a given particle. And do not provide any information about the orientation. One convenient parameter seems to be the ratio of the surface area to the projected (normal) area of the particle, $\chi$. Some prefer to express this ratio in terms of $d_s/d_n$ where $d_n$ is the diameter of the circle of area equal to the projected area of the particle. The shape factor combines all these attributes into a single parameter. The composite shape factor is:

\[
\chi = \frac{\text{surface area of particle}}{\text{projected area of particle}}
\]

Which can be rewritten in terms of sphericity as:

\[
\chi = \frac{\text{surface area of an equal volume sphere}/\psi}{\text{projected area of particle}}
\]

Now writing the two area terms in terms of $d_s$ and $d_n$:

\[
\chi = \frac{\pi d_s^2/\psi}{\pi d_n^2} = \frac{4}{\psi} \left( \frac{d_s}{d_n} \right)^2
\]  

(2.24)

The virtue of this parameter lies in its simplicity and in the fact that it combines the three attributes (size, shape, and orientation) into one composite shape factor. Table 2 lists values for $\chi$ for typical shapes.
Table 2 shows some counter-intuitive results. It is possible to obtain the same value of $\chi$ for two particles of different shape. It is possible to obtain values of $\chi$ lower than that for a sphere, $\chi=4$. Also, one would expect the drag on a cone falling point down to be less than a cone falling point up, but this approach does not distinguish between these two cases.

Figure 2 shows the predictions of equation (2.7) for non-spherical particles for a range of values. One can see that neither shape nor orientation seem to be important at low Reynolds number (predominantly viscous drag) and shape and orientation matter at high Reynolds number (major contribution from form drag).

Figure 2. Effect of particle shape and of power-law index on drag coefficients as predicted by equation (2.7)

3. **Transition: Particle/Particle Interaction, Hindered Settling, Packed Beds, Dispersions**

Settling behavior of a particle is strongly influenced by the presence of other neighboring particles as in concentrated suspensions.
**Hindered settling.** The terminal falling velocity of a sphere is influenced by the presence of neighboring particles. In concentrated suspensions, the settling velocity of a sphere is less than the terminal falling velocity of a single particle. For coarse (non-colloidal) particles in mildly shear-thinning liquids (0.8 ≤ n ≤ 1) the following expression for Newtonian fluids applies at values of Re up to about 2:

\[
\frac{V_0}{V} = (1 - C)^z
\]

(3.1)

Where \( V_0 \) is the hindered settling velocity of a suspension of uniform size spheres at a volume fraction \( C \), \( V \) is the terminal falling velocity of a single sphere in the same liquid, \( Z \) is a constant which is a function of the Archimedes number and \( d/D \) is given as:

\[
\frac{4.8 - Z}{Z - 2.4} = 0.0365 A_r^{0.57}[1 - 2.4(d/D)^{0.27}]
\]

(3.2)

Where for power-law fluids, the Archimedes number is \( A_r = C_D Re^{2(2-n)} \).

**Flow of liquid through particle beds.** Problems discussed so far relate to the motion of single particles in stationary non-Newtonian media. Consideration will now be given to the flow of non-Newtonian liquids through a bed of particles.

With downward flow of a liquid, no relative movement occurs between the particles except for that arising from their unstable initial packing. Pressure drop across the bed is directly proportional to the flow rate for Newtonian liquids and to the rate of flow raised to a lower (less than unity) exponent for a shear-thinning and to higher (>1) exponent for shear-thickening fluid. For upward flow through a bed which is not constrained at the top, the frictional pressure drop will be the same for the downward flow as long as the structure of the bed is not disturbed by the flow. Once the packing of the bed has reached its loosest stable form, any further increase in flow rate causes the individual particles to separate from one another and become freely supported in the liquid stream and the bed is said to be fluidized. With further increase in flow rate, the particles move further apart and the bed voidage increases while the pressure difference remains approximately equal to the buoyant weight per unit area of the bed. This is shown in Figure 3. Liquid fluidized beds continue to expand in a uniform manner, with a degree of agitation of particles increasingly progressively. Fluidization is then said to be particulate.
4. Rheology of Suspensions

4.1. Basics and Definitions

Suspensions and emulsions are types of dispersions.

A **Dispersion** consists of at least one solid or liquid phase (the disperse phase), which is dispersed in a liquid phase (the matrix phase). Both phases are immiscible.

**Suspensions** are materials that contain a granular solid material dispersed in a Newtonian or non-Newtonian matrix liquid. The rheological behavior of suspensions is very complex. Nonlinear flow behavior, normal stress differences, viscoelasticity, and yield stresses are some examples.

A **colloidal dispersion** is a system, in which particles of colloidal size of any nature (gas, liquid, solid) are dispersed in a continuous phase.

**Colloidal** refers to particles having at least one dimension in the size range 1nm to 1µm.

At the level of particles, dispersions can generally be classified concerning their size, size distribution, and the shape or shape distribution of the constituents of the disperse phase. All the most important properties in characterizing dispersions are shown in Table 3.

**Monodisperse** refers to a dispersion where all the particles are (nearly) the same size.

**Heterodisperse** dispersions have more than one discrete size particle distribution.

**Polydisperse** dispersions have many different sized particles.
Based on particle size, dispersions can be classified as shown in Figure 4.

**Table 3. Most important properties of dispersions.**

<table>
<thead>
<tr>
<th>Properties of the disperse phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle size and size distribution</td>
</tr>
<tr>
<td>Particle shape and shape distribution</td>
</tr>
<tr>
<td>Surface properties</td>
</tr>
<tr>
<td>Density viscosity, viscoelasticity (emulsions)</td>
</tr>
<tr>
<td>Surface energy</td>
</tr>
<tr>
<td>Particle volume concentration</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Properties of the continuous phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity, viscoelasticity</td>
</tr>
<tr>
<td>Aqueous, nonaqueous</td>
</tr>
<tr>
<td>Dissolved substances</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Properties of the interface</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electric double layer</td>
</tr>
<tr>
<td>ζ potential</td>
</tr>
<tr>
<td>Adsorption density</td>
</tr>
<tr>
<td>Thickness of the adsorbed layer</td>
</tr>
<tr>
<td>Structure of the adsorbed layer</td>
</tr>
</tbody>
</table>

4.2. Basic Assumptions

In static experiments gravity forces are in competition with the Brownian forces. The following ratio is used to estimate the sedimentation of samples:

\[
\frac{\text{gravity (settling) force}}{\text{Brownian (thermal) force}} = \frac{(\rho_d - \rho_c)ga^3}{k_B T/a}
\]  

(4.1)

Where \(\rho_d\) is the density of the disperse phase and \(\rho_c\) is the density of the continuous phase, \(g\) is gravity, \(a\) is particle radius, \(k_B\) is Boltzmann’s constant, and \(T\) is absolute temperature. If this ratio is greater than unity, sedimentation may occur. Typically, sedimentation takes place for \(\Delta \rho = \rho_d - \rho_c \approx 10^3 \text{kg/m}^3\) and for particles or aggregates larger than 1\(\mu\)m. Prior to rheometric
experiments, the tendency to sedimentation should be checked and if necessary, the experimental flow conditions should be adjusted so that during the experimental time the sedimentation does not play a role.

Beyond sedimentation, particle migration under flow conditions can also falsify measurements due to the resulting gradient in solid volume concentration inside the suspension. Normal force defects acting on particles can cause migration. Figure 5 (a) shows the symmetric normal forces, where no migration occurs. If shear flow is nonhomogeneous, the resulting force acts in the direction of decreasing shear rates and migration occurs. Nonhomogeneous shear flows should be avoided for correct measurement of viscosity.

![Figure 5. Hydrodynamic forces acting on a spherical (a) and nonspherical (b) particle in steady homogeneous shear flow and (c) on a spherical particle in nonhomogeneous shear flow.](image)

**Particle inertia** can also influence the results of transient or oscillatory experiments. If shear viscosity of the continuous phase is too small or if the particles are too heavy or too large, they cannot follow the unsteady external flow field. The particle Reynolds number is used as an estimation of inertial effects:

$\text{Re}_p = \frac{\rho \dot{\gamma} a^2}{\eta_c}$  

(4.2)

Where $\dot{\gamma}$ is the shear rate and $\eta_c$ is the viscosity of the continuous phase. Values of $\text{Re}_p$ approximately greater than $10^1$ indicate that particle inertia may be of relevance.
Finally, for all rheological measurements, it is necessary to ensure that the material can be regarded as a **continuum**. It is possible to regard the dispersion as a continuum when the length scales describing the motion of the suspension as a whole are much larger than the average size or average separation of the particles. It is a common rule that the maximum particle size must be at least one order of magnitude smaller than the smallest dimension of the measuring geometry.

Aggregation, agglomeration and Ostwald ripening can also occur.

### 4.3. Dimensional Analysis

The relevant physical quantities in suspension rheology are shown in Table 4.

<table>
<thead>
<tr>
<th>Property</th>
<th>Dimensional expression</th>
<th>Dimensionless group</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity</td>
<td>$\eta$</td>
<td>$\eta_t = \eta / \eta_c$ (relative viscosity)</td>
</tr>
<tr>
<td>Viscosity of the continuous phase</td>
<td>$\eta_c$</td>
<td>$\rho_t = \rho_d / \rho_c$ (density ratio)</td>
</tr>
<tr>
<td>Density of the disperse phase</td>
<td>$\rho_d$</td>
<td>$Re_p = \rho_c \gamma a^2 / \eta_c$ (particle Reynolds number)</td>
</tr>
<tr>
<td>Density of the continuous phase</td>
<td>$\rho_c$</td>
<td>$\xi$ (polydispersity measure)</td>
</tr>
<tr>
<td>Polydispersity</td>
<td>$\xi$ (dimensionless)</td>
<td>$\phi = \kappa (4\pi / 3) a^3$ (volume concentration)</td>
</tr>
<tr>
<td>Number density</td>
<td>$n$</td>
<td>$Pe = \eta_c \gamma a^3 / k_B T$ (Péclet number)</td>
</tr>
<tr>
<td>Particle radius</td>
<td>$a$</td>
<td>$\delta / a$ (relative surface layer thickness)</td>
</tr>
<tr>
<td>Gap width of the rheometer</td>
<td>$h$</td>
<td>$a / h$ (continuum parameter)</td>
</tr>
<tr>
<td>Adsorption layer thickness</td>
<td>$\delta$</td>
<td>$t_r = t / (\eta_c \gamma a^3 k_B T)$ (relative startup time)</td>
</tr>
<tr>
<td>Time</td>
<td>$t$</td>
<td>$Ga = \frac{(\eta - \eta_c) a^4}{k_B T}$ (settling parameter)</td>
</tr>
<tr>
<td>Acceleration of gravity</td>
<td>$g$</td>
<td></td>
</tr>
<tr>
<td>Thermal energy</td>
<td>$k_B T$</td>
<td></td>
</tr>
<tr>
<td>Dispersion (van der Waals) energy</td>
<td>$A_{\text{eff}}$</td>
<td>$\frac{A_{\text{eff}}}{\varepsilon e_0 \psi^2 a}$</td>
</tr>
<tr>
<td>Electrostatic energy</td>
<td>$\varepsilon e_0 \psi^2 a$</td>
<td></td>
</tr>
</tbody>
</table>

In general,

$$
\eta_t = f \left( \phi, \frac{\delta}{a}, \frac{a}{h}, \xi, \rho_t, t_r, Ga, Pe, Re_p, \frac{A_{\text{eff}}}{\varepsilon e_0 \psi^2 a} \right)
$$

(4.3)

For flow with small particle Reynolds number ($Re_p \ll 1$) within the continuum hypothesis ($a \ll h$), the relation reduces to:

$$
\eta_t = f \left( \phi, \frac{\delta}{a}, \xi, t_r, Pe \right)
$$

(4.4)
The Peclet number is the ratio between the shear force and the Brownian force. In other words, it is the ratio between order due to shearing and disorder due to Brownian motion. For suspensions with monodisperse unvarying particle size, (4.3) becomes,

$$\eta_r = f(\varphi, Pe)$$  \hspace{1cm} (4.5)

For highly dilute suspensions the relative viscosity depends solely on the solid volume concentration yielding a Newtonian behavior if the continuous phase is Newtonian:

$$\eta_r = f(\varphi)$$  \hspace{1cm} (4.6)

In contrast to the Peclet number given in table 3, the effective Peclet number is based on the macroscopic shear stress or the effective viscosity of the dispersion:

$$Pe_{eff} = \frac{\sigma a^3}{k_B T} = \frac{\eta \dot{\gamma} a^3}{k_B T}.$$  \hspace{1cm} (4.7)

4.4. Rheological Measurements

4.4.1. Influence of Solid Volume Concentration

The solid volume concentration is defined as:

$$\varphi = \frac{V_d}{V_c + V_d}$$  \hspace{1cm} (4.8)

Where $V_d$ is the volume of the disperse phase and $V_c$ is the volume of the continuous phase. Based on volume concentration, suspensions can be classified into three main categories: diluted, concentrated, and highly concentrated or solid suspensions. Generally, the flow depends on the shear rate or shear stress, respectively, the solid volume concentration, and the properties of the continuous phase.

Diluted suspensions show a Newtonian behavior. Einstein investigated the hydrodynamic forces resulting from the motion of the continuous phase with respect to noninteracting rigid spheres. He derived the equation:

$$\eta_r = \frac{\eta}{\eta_c} = 1 + k_1 \varphi + O(\varphi^2)$$  \hspace{1cm} (4.9)
For the viscosity of highly diluted suspensions in pure shear flow, with $k_1 = 2.5$ (called the Einstein coefficient). A generalized Einstein coefficient is the intrinsic viscosity, defined as:

\[
[\eta] = \lim_{\varphi \to 0} \frac{\eta_{\varphi} - 1}{\varphi} = \lim_{\varphi \to 0} \frac{\eta_{\text{sp}}}{\varphi}
\]

With $\eta_{\text{sp}}$ as the specific viscosity. It is applicable for suspensions of spherical particles with solid volume concentrations up to $10^{-2}$.

A further increase of $\varphi$, the transition from dilute to concentrated, causes increasing interactions of the hydrodynamic fields between spheres or aggregates. Extending Einstein’s equation to higher concentrations:

\[
\eta_{\varphi} = 1 + k_1 \varphi + k_2 \varphi^2 + O(\varphi^3)
\]

Where $k_2$ describes the deviation from the very dilute limit of the suspension. This equation holds for $\varphi$ up to $2 \times 10^{-1}$.

This series can be summarized in a general equation for the dependence of the relative viscosity on $\varphi$ with $k_i$ as the concentration independent expansion coefficients:

\[
\eta_{\varphi} = \sum_{i=0}^{N} k_i \varphi^i
\]

The relative viscosity in equation (4.12) represents both shear and elongational viscosities.

Coefficients of some useful models are shown in Table 5.

Table 5. Models describing the dependence of the viscosity on the solid volume concentration for moderately concentrated suspensions.

<table>
<thead>
<tr>
<th>Source</th>
<th>$N$</th>
<th>$k_0$</th>
<th>$k_1$</th>
<th>$k_2$</th>
<th>$k_3$</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>[9.210,211,216]</td>
<td>1</td>
<td>1</td>
<td>2.5</td>
<td>-</td>
<td>-</td>
<td>$\varphi &lt; 0.01$</td>
</tr>
<tr>
<td>[9.213]</td>
<td>2</td>
<td>1</td>
<td>2.5</td>
<td>7.6 (elongation)</td>
<td>-</td>
<td>$\varphi &lt; 0.2$</td>
</tr>
<tr>
<td>[9.214]</td>
<td>3</td>
<td>1</td>
<td>2.5</td>
<td>5.2 (shear)</td>
<td>6.2</td>
<td>$\varphi &lt; 0.2$</td>
</tr>
<tr>
<td>[9.217]</td>
<td>3</td>
<td>1</td>
<td>2.5</td>
<td>4.94</td>
<td>15.7</td>
<td>$\varphi &lt; 0.3$</td>
</tr>
<tr>
<td>[9.218]</td>
<td>3</td>
<td>1</td>
<td>2.5</td>
<td>6.25</td>
<td>15.7</td>
<td>$\varphi &lt; 0.3$</td>
</tr>
<tr>
<td>Low-shear limit</td>
<td>3</td>
<td>1</td>
<td>2.5</td>
<td>$4 \pm 2$</td>
<td>42 ± 10</td>
<td>$\varphi &lt; 0.35$</td>
</tr>
<tr>
<td>High-shear limit</td>
<td>3</td>
<td>1</td>
<td>2.5</td>
<td>$4 \pm 2$</td>
<td>25 ± 7</td>
<td>$\varphi &lt; 0.35$</td>
</tr>
</tbody>
</table>

For higher solid volume concentrations, where hydrodynamic and surface force interactions as well as many-body interactions become relevant, the power series expansion fails since the viscosity tends to infinity at solid volume concentrations in the
vicinity of the maximum packing fraction. The **maximum packing fraction** is a characteristic scalar value that mainly depends on the particle size distribution, particle shape distribution, type of the interactions between the disperse and continuous phases, and the shear intensity. Table 6 shows theoretical values for the maximum packing fraction for common arrangements. If the solid volume concentration approaches the maximum packing fraction, a transition from liquid- to solid-like behavior occurs.

Table 6. Maximum packing fractions for regular arrangements of monodisperse spherical particles.

<table>
<thead>
<tr>
<th>Type of packing</th>
<th>Maximum packing fraction $\varphi_{\text{max}}$ (theoretically from geometry)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Face-centered cubic (fcc)</td>
<td>$\sqrt{2}/6 = 0.7405$</td>
</tr>
<tr>
<td>Body-centered cubic (bcc)</td>
<td>$\sqrt{3}/8 = 0.6802$</td>
</tr>
<tr>
<td>Random closed</td>
<td>0.6370</td>
</tr>
<tr>
<td>Hexagonal</td>
<td>$\sqrt{3}/9 = 0.6046$</td>
</tr>
<tr>
<td>Simple cubic</td>
<td>$\pi/6 = 0.5236$</td>
</tr>
<tr>
<td>Diamond</td>
<td>$\sqrt{3}/16 = 0.3401$</td>
</tr>
</tbody>
</table>

Under shear the arrangement of the particles in the fluid is modified, so that the maximum packing fraction depends on the shear rate or shear stress applied. A simple model to describe the shear dependent maximum packing fraction is the following relation:

$$\frac{1}{\varphi_{\text{max}}(\sigma)} = \frac{1}{\varphi_{\text{max},0}} - \left( \frac{1}{\varphi_{\text{max},0}} - \frac{1}{\varphi_{\text{max},\infty}} \right) S(\sigma)$$

(4.13)

The $\varphi_{\text{max}}$ values are the maximum packing fractions in the low- and high-shear rate limit. The function $S$ can be interpreted as a scalar structural parameter with values between 0 and 1 depending on shear stress. The following has been proposed:

$$S(\sigma) = \frac{1}{1 + K \sigma^{-m}}$$

(4.14)

The parameters $K$ and $m$ must be evaluated by fitting experimental data.

At higher shear rates, highly concentrated suspensions with solid volume concentration of 50% and higher may show shear thickening. This effect is caused by a more or less sudden change in the microscopic structure of the suspension. At high volume concentrations a shear thinning region can also be observed which passes into a region with increasing viscosity at a **critical shear rate**, $\dot{\gamma}_{\text{cr}}$. 
A correlation between the particle size and the critical shear rate is:

\[ \dot{\gamma}_{cr} (a) = Ka^{-2} \quad (4.15) \]

With the value of \( K \approx 4 \mu m^2/s \) obtained from a rough fit of data.

The effect of shear thickening does not only occur in steady shear experiments. It has been observed in so-called strain thickening in oscillatory shear flows. A critical combination of a shear strain and an angular frequency exists where the complex viscosity sharply increases. Two different cases are possible: high critical strains at low frequencies and high critical frequencies at low strains. In the first case, the correlation is:

\[ |\eta^*(\dot{\gamma}; \omega)| = \eta(\dot{\gamma})\bigg|_{\omega=\dot{\gamma}} \quad (4.16) \]

Where \( \dot{\gamma} \) is the shear strain amplitude.

### 4.4.2. Choice of Measurement Geometry

Before performing the rheological measurement of a suspension, it is important to choose a suitable measurement geometry. The choice depends on the expected rheological properties of the suspension. It is possible to choose a suitable geometry based on the following:

1. the shear rate or shear stress range of interest – stability of flow in the range of interest
2. the existence of a possible yield stress, as well as the order of magnitude of the viscosity and/or normal stress differences
3. the possibility, to prevent wall slip or, if this is not possible, to detect and correct for wall slip

The cone-and-plate (CP) system is suitable for low and medium shear rates. Especially at higher concentration, the flow in CP systems becomes unstable due to shear fracture. Independent of instability problems, the CP system with small cone angles (\( \leq 4^\circ \)) is the most preferable geometry for the investigation of suspensions because the shear rate and the shear stress are approximately constant over the whole sample. CP geometry allows for the determination of the first normal stress difference from the axial force, easily measured by modern rheometers.
Similar sample instabilities can be observed in torsional plate-plate (PP) geometries. The PP system is unsuitable for rheological measurements of non-Newtonian suspensions due to the strong inhomogeneous shear field in the gap. Torsional PP geometry is a necessary tool for the measurement of the difference between the first and second normal stress difference.

**Sedimentation** or demixing effects influence the experimental results obtained in CP and PP geometries to a major degree. Demixing effects can manifest as an untypical time-dependent decrease of the viscosity, which in the case of a Newtonian continuous phase, tends towards the viscosity of the continuous phase. This effect can be misinterpreted as shear thinning. To estimate the influence of settling based on the balance between Stokes force, the gravitational force, and the buoyant force, and equation can be derived to estimate the time required for a single sphere to migrate over length L:

\[
\frac{9}{2} \frac{\eta_c}{\Delta \rho g a^2} \quad (4.17)
\]

With \( t_{\text{exp}} \) as the experimental time.

If smaller particles are used, the possible density difference between particles and liquid increases quadratically. Settling time increases if the solid volume concentration is high enough that hindered settling occurs or if a superposed shear flow during measurement is realized. Generally,

\[
\frac{2}{9} \frac{t_{\text{exp}} \Delta \rho g a^2}{\eta_c h} \ll 1 \quad (4.18)
\]

Must be fulfilled to neglect the influence of settling.

The problems discussed with CP and PP geometries can be at least partially avoided if **coaxial cylinders** are used since the gravity acts parallel to the cylinder gap. Sedimentation is not as dramatic as described for CP and PP, however, sedimentation leads to depletion of particles in the shear gap and hence to an initial decrease of the viscosity. If the solid volume concentration is high enough, a compact layer of solid is generated at the bottom of the outer cylinder. This observation can be misinterpreted as shear thickening.

One of the most well-known problems arising in experimental investigations of suspensions is **wall-slip**. There are two different types. The first type. True wall slip, has
been found with unfilled polymers. This effect is generally associated with the flow instabilities during the extrusion process. True wall slips is only of relevance when dealing with polymers.

With moderately and highly concentrated suspensions, the second type, an apparent wall slip effect, can occur which is caused by particle migration. The flow induced forces cause a movement of the particles from regions of higher (near wall) to regions of lower shear rates. This effect results in a solid volume concentration distribution over the sample. A criterion for neglecting migration effects that compares the inertial effects and Brownian motion is:

\[ K = \frac{\rho \bar{u}^2 d^4}{h k_B T} \begin{cases} < 0.1 & \text{Couette flow} , \\ < 0.01 & \text{plane Poiseuille flow} . \end{cases} \] (4.19)

Where \( \bar{u} \) is the mean velocity in the gap (Couette flow: \( \bar{u} = \frac{1}{2} u_{\text{max}} \), and Poiseuille flow: \( \bar{u} = \frac{2}{3} u_{\text{max}} \)) and \( h \) is the gap width. The danger of migration strongly increases with the particle size, since the influence of the thermal forces decreases with increasing size. Shear induced particle migration is typically negligible for length-to-diameter (or gap) ratios of 0-50 provided that the ratios of particle-to-tube (or channel gap) radii are \( 5 \times 10^3 \) and smaller. Under these conditions, the wall concentration is within 2% of the initial concentration of the suspension in the solid volume concentration range \( 0.1 \leq \phi \leq 0.5 \).

From rheological measurements, the thickness of the slip layer could be estimated by:

\[ \delta_S = \frac{\bar{u}_S \eta_S}{\sigma} \] (4.20)

With \( u_S \) as the slip velocity obtained from a plot of the apparent shear rate at the rim of the PP geometry as a function of the inverse gap height. To avoid wall slip caused by particle migration, it is necessary to disrupt the slip layer. This can be achieved by serrated or roughened measurement systems. The roughness must be larger than the slip layer thickness. Generally it is possible to correct the effect of wall slip if Couette device with two different inner radii, cylinders, and outer cylinders are used. The wall slip velocity can be calculated by using the formula:

\[ u_S(\sigma) = \frac{\beta}{\beta + 1} \left( \frac{\Omega_1 - \Omega_2}{R_{i,1}^{-1} - R_{i,2}^{-1}} \right) \] (4.21)
For the Couette device with $\beta-1<<1$ (small gaps), where $\sigma_i$ is the same shear stress at the inner cylinder for the two independent measurements with angular speeds $\Omega_1$ and $\Omega_2$. The true shear rate at the wall in the two cylinder system can then be obtained:

$$\dot{\gamma}_{i,a} = \dot{\gamma}_1(\sigma_i) + \frac{2u_s(\sigma_i)}{R_i} \tag{4.22}$$

For torsional plate-plate geometries the slip velocity is:

$$u_s(\sigma_R) = \frac{\dot{\gamma}_{aR,1}(\sigma_R) - \dot{\gamma}_{aR,2}(\sigma_R)}{2\left(h_1^{-1} - h_2^{-1}\right)} \tag{4.23}$$

And the true shear rate at the walls can be calculated by:

$$\dot{\gamma}_{aR} = \dot{\gamma}_R(\sigma_R) + \frac{2u_s(\sigma_R)}{h} \tag{4.24}$$

Finally, some conditions which usually lead to significant wall slip effects are:

- large particles in the disperse phase (including flocs or aggregates)
- a strong dependence of viscosity on the solid volume concentration of the disperse phase
- smooth walls (sandblasted walls or profiled cones, plates or cylinders can prevent wall slip, but can lead to shear fracture)
- small flow dimensions
- usually low speeds/flow rates
- walls and particles with electrostatic charges while the continuous phase is electrically conductive.