Sample Chapter 4:
Dispersive Mixing of Solid Additives
4 Dispersive Mixing of Solid Additives

Ica Manas-Zloczower and Donald L. Feke*

This chapter reviews some of the existing models for the dispersion of solid fine particle clusters into high viscosity liquid media. Due to the complexity of the process, none of these models depicts perfectly all aspects of dispersion. However, each and every one of them provides the grounds for a better understanding of mixing phenomena.

Most of the existing theoretical models focus on the competitive forces involved in dispersion, namely the forces of cohesion within the clusters and the hydrodynamic forces inducing their breakup. Agglomerate cohesivity is usually related to either the interparticle forces or to the energy of fracture. Simple phenomenological models based on experimental observations on dispersion phenomena in well-defined flow fields are also presented. Such models point out the most important factors governing the mechanisms and kinetics of the process.

The models in this chapter are presented in a somewhat chronological order, reflecting the advances made in the understanding of dispersion phenomena. Their use in predictive studies depends primarily on the experimental and computational tools available for system characterization.

4.1 Introduction

Many additives used in the plastics and rubber industry are colloidal in nature and exist in the form of aggregates composed of primary particles permanently fused together. In turn, aggregates cluster together under the influence of surface forces in collections of aggregates, referred to as agglomerates. A typical example is carbon black, with aggregates on the order of 0.1 μm in size and agglomerates in the range of 10–100 μm and up.

The polymer compounding always starts with carbon black in the form of pellets of the order of a few tenths of a millimeter in size – that is, 1000 times as large as the aggregates. In an ideal mixing operation, all carbon black pellets/agglomerates would be dispersed into aggregates, uniformly distributed throughout the polymeric matrix. There are several stages involved in any dispersive mixing operation. Parfitt [1] identified four steps in the process of dispersion of powders in liquid media:

- incorporation of powder into liquid;
- wetting of the powder;
- breaking up of agglomerates and possibly aggregates; and
- stabilization of the resulting dispersion.

Author:

Please carefully check all equations and special symbols because conversion errors may have occurred. Also, make sure notations of matrices, tensors, vectors etc. are consistent in your chapter and agree with your symbol list.

- variable: italic
- counter: italic (typical letters: i, j, k, l, m, n)
- vector, matrix: bold-italic
- tensor: bold
- unit: regular (typical examples: cm, mm, μm, kg, kN ...)
- constant: regular (typical examples: Euler constant “e” and “π” in use of 3.14 ...)
- differential operator: regular (typical examples: “d”, “D” and “i”)
- index (subscript, superscript): regular if in use of description (if in use of counter or variable: italic)
For the dispersion of carbon black agglomerates into rubber, Medalia [2] classified the stages of a mixing operation as

- incorporation, involving wetting of the pellets by the polymer;
- deagglomeration by breaking the agglomerates;
- distribution of the agglomerates and aggregates throughout the polymer by random patterns of flow; and
- flocculation, involving diffusion and cohesion of aggregates into a network.

Tokita and Pliskin [3, 4] took a slightly different point of view and identified only three stages in mixing carbon black and rubber:

- filler wetting (or induction);
- filler dispersion (or agglomerate breakdown); and
- elastomer breakdown and interaction with filler.

In any of the foregoing classifications, incorporation is the first step of mixing. At the end of this step, the loose filler particles disappear, and all the air, introduced in the compound by entrapment with the agglomerates, has been replaced by the polymeric media. The polymer wets the filler and it may penetrate into the void spaces of the agglomerate and also within the aggregates. Medalia [5] has proposed that in a carbon black-rubber system, the rubber that penetrates within the aggregates is occluded and immobilized and thus acts as part of the filler rather than as part of the matrix. The concept of immobilized occluded rubber has been used by several authors to account for the effect of carbon black on rubber properties such as die swell [5], modulus [6–8], and tensile strength and road-wear [9].

In the next step of the mixing process, dispersion, the agglomerates are broken into smaller fragments, down to aggregate size. It is generally recognized that this is the most difficult step and therefore the rate-determining one in any mixing operation. A detailed discussion on this stage of mixing is the main subject of this chapter.

Once the filler agglomerates have been broken, separation of the closely spaced fragments and their distribution throughout the polymeric matrix should be accomplished. In the fragment separation step, flow kinematics becomes important [10].

An interesting phenomenon, reversing some of the effect of the dispersion process, is flocculation [2]. This process contributes to the formation of a filler network throughout the matrix. In the case of the carbon black-rubber system, the presence of such a network explains the electrical conductivity and dynamic mechanical properties of the compound.
4.2 Continuum Dispersion Models

The dispersion of solid agglomerates in liquid media is a complex process and therefore any attempt to model it will always contain simplifications. Modeling, however, not only allows a better understanding of the process, but also permits the effects of various individual variables on dispersion to be isolated and studied.

Most of the existing dispersion models consider the breakup of agglomerates to be the most important step in mixing. Bolen and Colwell [11] were the first to propose that rupture occurs when internal stresses, induced by viscous drag on the agglomerates, exceed a certain threshold value. Following their lead, several authors [12–17] extended the analysis of agglomerate rupture and developed various models for the mixing process, which generally evolved in their degree of sophistication. Because of the complexity of the process, however, none of these models perfectly depicts all aspects of dispersion. Yet, each and every one of them sheds light on the role of various material and process parameters in the dispersion process and provides some theoretical background for a better understanding of the mixing phenomena.

4.2.1 Agglomerate Structure and Cohesiveness

Most of the present models for agglomerate strength [18–21] treat the structure of the agglomerate very simply, usually as a uniformly porous sphere or as a uniform assembly of spheres. One notable exception is the work of Sonntag and Russel [22], who modeled agglomerates of polystyrene latex spheres as homogeneous porous spheres with a position-dependent internal structure. The internal volume fraction within the floc $\phi(r)$, at a local position $r$ with respect to the center of mass, varies as $\phi \propto r^{D_f - 1}$, where $D_f$ is the fractal dimension of the floc. Accordingly, the elastic shear modulus $m$, and the bulk modulus $l$, which vary with volume fraction as $\phi^n$, will also depend on the position $r$ within the floc. However, effects of fluctuations in volume fraction due to the presence of structural heterogeneities, intrinsic to real structures, are ignored.

The presence of structural heterogeneities within the agglomerates is of extreme significance in the dispersion process, since such anomalies could be uncharacteristically weak portions of the agglomerate (which are the sites at which breakup could initiate), or uncharacteristically strong portions of the agglomerate (which would be the most difficult portions of the agglomerate to disperse). Horwatt and co-authors [23] developed a method to analyze the influence of agglomerate structure on its dispersion in a simple shear flow field. They assumed that the strength of the interparticle bonds is uniform throughout the agglomerate and that in order to detach the fragment, all bonds connecting a given fragment to the cluster must be severed simultaneously. The authors simulated a number of different fractal (diffusion-limited, reaction-limited, and hierarchical cluster-cluster agglomerates) and non-fractal (linear trajectory agglomerates and Eden model growth clusters) structures. They searched through the different structures and identified the fragment requiring the lowest stress to break up. Such fragments were designated as critical fragments and they determined the overall cohesivity of the agglomerates.
Given or assuming an agglomerate structure, there are various models to calculate its strength. Most of the existing models relate the tensile strength of the agglomerate to the interparticle forces. One of the first models was developed by Rumpf [18], who derived a number of expressions for strength by focusing on the various mechanisms of particle adhesion (van der Waals forces, liquid bridges, solid binding, etc.). Rumpf based his model on certain important assumptions:

- there are a large number of bonds in the fracture section;
- the bonds are randomly distributed over the fracture section and have random orientation in space;
- the particles in the agglomerate are randomly distributed in space; and
- all interparticle forces can be considered in terms of a single mean effective force.

For equal-sized spherical particles Rumpf derived an expression of the form:

\[ T = \frac{9}{8} \pi d^2 c F (4.1) \]

where \( T \) is the tensile strength, \( d \) is the diameter of the spherical particle, \( \varepsilon \) is the void volume fraction within the total volume, \( c \) is the mean coordination number, defined as the mean number of particles touching a given one, and \( F \) is the mean interparticle force.

An independent study on the tensile strength of powder compacts along similar lines has been made by Cheng [19, 24, 25]. Like Rumpf, Cheng assumes that in a powder compact, individual particles are packed together in a more or less random fashion. The particles are taken to have an average coordination number, and the tensile strength is taken to be an average over a large number of particle pairs in the fracture plane. The equation for the tensile strength of dry powder compacts is:

\[ T = \frac{3}{4} H^0 \frac{d^5}{\rho} \frac{\rho_s}{1 - (\rho / \rho_s)} F_{pp}^0 (4.2) \]

where \( H^0 \) is the effective surface separation distance at zero tensile strength; \( d, s, \) and \( v \) are the mean particle diameter, surface area, and volume, respectively; \( \rho \) is the bulk density; \( \rho_s \) the density of the particles; and \( F_{pp}^0 \) is the interparticle force per unit fracture area.

Hartley and Parfitt [20] derived an expression for the tensile strength of a powder compact composed of individual, spherical particles of uniform, submicrometer size, packed in a random fashion:

\[ T = \frac{9}{4} \frac{(d + t)(t_0 - t)}{d^2} \frac{\rho / \rho_s}{1 - (\rho / \rho_s)} F_{pp}^0 (4.3) \]

where \( d \) is the diameter of the spherical particles, \( t \) is the apparent separation distance between particle surfaces (related to particle diameter and powder packing density), \( t_0 \) is the apparent
Models in a different category relate the tensile strength of agglomerates to the energy of fracture. Sonntag and Russel [22] modelled the agglomerate as a slightly deformable porous sphere and used the Mises yield criterion to predict rupture. The floc ruptures when the local energy of distortion $U$ exceeds a critical value $U_c$. The local energy of distortion is calculated from:

$$U = \frac{\sigma_D^2}{4m}$$ (4.4)

where $\sigma_D$ is the deviatoric part of the stress tensor and $m$ is the floc elastic shear modulus. Kendall [26] proposed a model of agglomerate strength based on a fracture mechanics approach, in which the agglomerate is viewed as an elastic body that satisfies the Griffith energy criterion of fracture. The agglomerate tensile strength can be calculated from:

$$T = 15.6 \phi^4 \Gamma_c^{5/6} \chi^{1/6} (d \alpha)^{-1/2}$$ (4.5)

where $\phi$ is the solid volume fraction, $\Gamma_c$ is the fracture energy, $\chi$ is the interfacial energy between the elastic spheres of diameter $d$ packed into the cluster, and $\alpha$ is the length of a macroscopic flaw in the agglomerate from which fracture is initiated.

The use of any of the theoretical models presented here for the calculation of agglomerate cohesivity depends primarily on the availability of experimental data for the parameters used in these models. In general one should identify the model that fits best the available experimental data and use that model in predictive studies for agglomerate cohesivity. Characterization of agglomerate structure, especially in terms of internal degree of connectivity, is equally important, especially for the more advanced dispersive mixing studies.

### 4.2.2 Models for Agglomerate Dispersion

In developing an analysis of agglomerate dispersion by an applied flow field, agglomerate structure and cohesivity, as well as the effect of the applied hydrodynamics on the mechanics of the agglomerates must be considered.

One of the models for agglomerate hydrodynamic analysis defines the cluster as two touching rigid spheres of radii $R$ and $\Lambda R$, with $0 \leq \Lambda \leq 1$ and having a total volume equal to that of the agglomerate. Nir and Acrivos [27] calculated the net hydrodynamic force acting on the larger of the two spheres, $F_h$, where both are freely suspended:

$$F_h = \pi \mu R^2 \dot{\gamma} [h_1(\Lambda) E \cdot n + h_2(\Lambda) mn \cdot E \cdot n]$$ (4.6)

In Eq. (4.6), $\mu$ is the viscosity of the suspending fluid, $E$ is the rate of deformation tensor for the applied flow field scaled on the applied shear rate $\dot{\gamma}$, and $n$ is the unit vector pointing along the line of centers between the two spheres. The scalars $h_1$ and $h_2$ are functions of the
size ratio $\Lambda$, of the touching spheres, and are at maximum for equal-sized spheres [27], indicating that the effect of hydrodynamic tension would be largest for an agglomerate being split into equal halves.

The kinematics of agglomerates, modelled as two non-touching spherical fragments, in linear flow fields can be analyzed in terms of the theory developed by Batchelor and Green [28] and can be described by the dimensionless equation:

$$v = \omega \times r + E \cdot r - \left[ A(r, \Lambda) \frac{Tr}{r^2} + B(r, \Lambda) \left( I \frac{Tr}{r^2} \right) \right] \cdot E \cdot r$$

(4.7)

where $v$ is the velocity vector describing the motion of one sphere relative to the other, scaled on $a \gamma$, $r$ is the position vector connecting the centers of the two spheres made dimensionless on the sphere radius $a$, $\omega$ is the vorticity vector scaled on $\gamma$, $I$ is the identity tensor, and $r$ is the magnitude of vector $r$. The functions $A(r, \Lambda)$ and $B(r, \Lambda)$ are mobility functions that characterize the hydrodynamic interactions between the spheres [28]. Equation 4.7 is used in conjunction with Eq. (4.6) to predict the hydrodynamic interaction as the agglomerate rotates in the linear flow field. Rupture occurs at the contact point between the two spheres when the hydrodynamic tension acting to separate the agglomerate exceeds the cohesive force within the agglomerate.

Combining Rumpf’s model for the agglomerate cohesive strength with the hydrodynamic analysis for two touching rigid spheres described above, Manas-Zloczower, Nir, and Tadmor [17, 32] derived a model for agglomerate dispersion in simple shear flow. The fraction of agglomerates broken by the applied flow field was found to be dependent on a dimensionless parameter $Z$ given by:

$$Z = \frac{\chi \mu \gamma}{T}$$

(4.8)

where $\chi$ is the scalar reflecting the geometry of the breakup process, $\mu$ is the velocity of the suspending fluid, $\gamma$ is the applied shear rate, and $T$ is the tensile strength of the agglomerates. The parameter $Z$ scales the magnitude of the forces acting to rupture the agglomerate relative to the tensile strength of the agglomerate and is independent of the absolute size of the cluster. Agglomerate breakup was modeled as a repetitive process. Cleavage of the agglomerate was predicted to occur at the mid-plane, where the effect of hydrodynamic tension would be largest. A random distribution of orientations of the fracture surface among the agglomerates at the start of the flow or at the time of their formation was assumed. The dynamics of agglomerate size distribution was also predicted.

An extension of this model for various (linear) flow geometries was proposed by Manas-Zloczower and Feke [33]. For each flow geometry there is a minimum value of the parameter $Z$ required for rupture to occur. This value corresponds to the condition at which the hydrodynamic tension acting to separate the agglomerate exceeds the cohesive force within the agglomerate for a fracture plane oriented perpendicular to the principal axis of strain for each flow field. The range of values of $Z$ that lead to agglomerate rupture for the flow fields investigated is:
4.2 Continuum Dispersion Models

Simple shear $Z \geq 2$
Pure elongation $Z \geq 1$
Uniaxial extension $Z \geq 1/2$
Biaxial extension $Z \geq 1$

The model was analyzed for hypothetical systems characterized by different values of the parameter $Z$. The fraction of agglomerates broken at a certain time of shearing corresponds to the fraction of initial angular orientations of the fracture plane for which the condition of agglomerate breakup is fulfilled from the start of the flow until to the given time. The results obtained for agglomerate lifetime were also used to determine the dynamics of particle size distribution produced from the parent agglomerates. At any time $t$, the agglomerate size distribution in the volume element can be expressed in terms of rates of formation and rupture for different agglomerate sizes. Assuming that at the start of flow only agglomerates of size $D_0$ are present, the total amount of $i$-sized agglomerates (agglomerates formed after $i$ consecutive breakings) present initially and formed by the rupture process $W_i$ is given by the system of kinetic equations:

$$W_i(t) = G(t) \quad i = 0$$
$$W_i(t) = \int_{t^*=0}^{t} \frac{dW_{i-1}}{dt^*} F(t - t^*) \, dt^* \quad i = 1, 2, \ldots, n$$

where $G(t)$ is the Heaviside function and $F$ is the fraction of agglomerates broken as a function of time. The net fraction of $i$-sized agglomerates present in the volume element at any time, $Y_i$, is given by the difference between the fraction created and the fraction destroyed:

$$Y_i = \begin{cases} W_i - W_{i+1} & i = 0, 1, \ldots, n - 1 \\ W_i & i = n \end{cases}$$

where $n$ is the maximum number of consecutive breakings for agglomerates of initial diameter $D_0$. Figures 4.1–4.4 show the dynamics of agglomerate size distribution in the various flow fields investigated for the same value of the parameter $Z$. The predicted population distributions are qualitatively similar for the three elongational flow fields, but because of the nonzero vorticity, they are quite different for the simple shear flow.

Another model for the hydrodynamic stress acting on agglomerates in linear flow fields can be derived using concepts originally suggested by Bagster and Tomi [29]. Agglomerates are viewed as homogeneous spheres undergoing bulk motion as single entities, and neglecting the fluid interstitial velocity through the clusters. For low Reynolds number flows, the hydrodynamic stress acting on the cluster surface can be written in the form [30]:

$$\sigma = 5 \mu \left( \mathbf{E} : \mathbf{r} \right)$$

where $\mathbf{E}$ is the rate of the strain tensor for the bulk flow field, and $\mathbf{r}$ is the orientation vector relative to the sphere center. The approach taken to examine the stresses within the sphere is to consider any plane that divides the sphere into two portions. The fluid surface forces induce
Figure 4.1: Evolution of the agglomerate size distribution in simple shear flow for the case of $Z = 10$: volume fraction of agglomerates of various sizes shown as a function of the dimensionless time of shearing.

Figure 4.2: Evolution of the agglomerate size distribution in uniaxial extensional flow for the case of $Z = 10$.
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Figure 4.3: Evolution of the agglomerate size distribution in biaxial extensional flow for the case of $Z = 10$

Figure 4.4: Evolution of the agglomerate size distribution in pure elongational flow for the case of $Z = 10$
a total force on each of the two portions, from which a net hydrodynamic force on the plane can be computed. As sketched in Fig. 4.5, the orientation of the unit vector normal to the plane, \( \mathbf{n} \), with respect to the flow field is described by the polar angle \( \theta \) and azimuthal angle \( \phi \). The portion of any plane having the unit normal vector \( \mathbf{n} \) can be specified by an angle \( \psi_{0} \), which gives the intersection of the plane with the cluster surface (Fig. 4.5).

Scurati [34] developed a model of dispersion based on the assumption that the likelihood of erosion (\( L_{e} \)) for a position (likewise a plane) identified by an angle \( \theta, \phi \) (Fig. 4.5) of an agglomerate is proportional to the excess forces (difference between hydrodynamic force \( F_{h} \) and cohesive force \( F_{c} \)) at that location

\[
L_{e}(\theta, \phi, t) \propto F_{h} - F_{c} \tag{4.12}
\]

Considering a non-fractal agglomerate, both \( F_{h} \) and \( F_{c} \) scale with the surface of the plane of failure. Thus, Eq. (4.12) can be rewritten in terms of stresses:

\[
L_{e}(\theta, \phi, t) \propto \sigma_{e}(fa - 1) \tag{4.13}
\]

where \( fa \), defined as an actual fragmentation number is the ratio of the hydrodynamic and cohesive forces at a given point in space and time.

The local rate of erosion \( E(\theta, \phi, t) \) is the product of the likelihood of erosion with a frequency factor indicating the renewal velocity of the flow field, meant to represent a frequency at which new agglomerate surface is exposed to hydrodynamic forces. In the case of a simple shear flow, this can be easily identified with the rotation velocity of the agglomerate \( \gamma/2 \)

\[
E(\theta, \phi, t) \propto (fa - 1) \gamma \tag{4.14}
\]

In Eq. (4.14), \( \sigma_{e} \) and the other constants were included in the proportionality factor.

To monitor the erosion history of a particular point \( \theta_{0}, \phi_{0} \) (or likewise of a particular plane) on the agglomerate surface, one can derive the local time average rate of erosion over one cycle, taking into account the motion of the agglomerate in the flow field.

\[
\langle E(\theta_{0}, \phi_{0}) \rangle_{\tau} \propto \frac{1}{\tau} \int_{0}^{\tau} E(\theta(\theta_{0}, \phi_{0}, t), \phi(\theta_{0}, \phi_{0}, t), t) \, dt \tag{4.15}
\]

where \( \theta(\theta_{0}, \phi_{0}, t), \phi(\theta_{0}, \phi_{0}, t) \) indicate the motion of the point that start (at time \( t = 0 \)) at position \( \theta_{0}, \phi_{0} \).

In order to make the erosion history analysis independent of the particular fluid viscosity used in the definition of the fragmentation number, one can derive the strain average extent of erosion for one point in one cycle.

\[
\langle E(\theta_{0}, \phi_{0}) \rangle_{\gamma} \propto \frac{\int_{0}^{\tau} E(\theta(\theta_{0}, \phi_{0}, t), \phi(\theta_{0}, \phi_{0}, t), t) \, dt}{\int_{0}^{\tau} |\dot{\gamma}| \, dt} \tag{4.16}
\]
The term \( \langle E(\partial_0, \varphi_0) \rangle_\gamma \) in Eq. (4.16) can also be considered a dimensionless time rate of erosion.

This is a measure of the erosion history of one point during one period. The specific period \( \tau \) depends on the flow field and system considered. The overall surface average of the erosion rate (namely \( E(t) \)), of the time average erosion rate (\( \langle E \rangle_\tau \)) and of the dimensionless time erosion rate (\( \langle E \rangle_\gamma \)) can be derived by doing a surface average of Eqs. (4.14), (4.15) and (4.16).

\[
E(t) = \frac{\int E(\partial, \varphi, t) \, dS}{\int dS} \quad (4.17)
\]

\[
\langle E \rangle_\tau = \frac{\int \langle E(\partial, \varphi) \rangle_\tau \, dS}{\int dS} \quad (4.18)
\]

\[
\langle E \rangle_\gamma = \frac{\int \langle E(\partial, \varphi) \rangle_\gamma \, dS}{\int dS} \quad (4.19)
\]

Evidence of weaker cohesive strength in tensile rather than in shear allows for limiting the calculations to the normal hydrodynamic forces. Therefore, the likelihood to erosion (\( L_e \)) and the local erosion rate for an impermeable spherical agglomerate in a simple shear flow can be derived assuming the expression for the normal components of the hydrodynamic forces as calculated by Bagster and Tomi [29].

\[
L_e(\partial, \varphi, t) \approx \left( \frac{5}{4} \mu \dot{\gamma}(t) \sin^2 \theta \sin 2 \varphi - \sigma_c \right) \propto f_a - 1 \quad (4.20)
\]

\[
E(\partial, \varphi, t) \approx \left( \frac{5}{4} \mu \dot{\gamma}(t) \sin^2 \theta \sin 2 \varphi - \sigma_c \right) \frac{\dot{\varphi}}{2} \propto (f_a - 1) \frac{\dot{\varphi}}{2} \quad (4.21)
\]

where \( f_a \) is the actual fragmentation number experienced by a point \( \partial, \varphi \) at time \( t \). For the calculation of the erosion history one needs to take into consideration agglomerate motion. Looking at the coordinate system chosen (Fig. 4.5), one recognizes that the agglomerate motion can be identified with the angle \( \varphi \) (which lays on the \( y-x \) plane and therefore is the only coordinate changing). Therefore, in a simple shear flow, the motion of a point on the agglomerate surface starting at position \( \partial_0, \varphi_0 \) can be described as:

\[
\varphi(t) = \varphi_0 + \int_0^t \dot{\varphi} \, dt
\]

\[
\theta(t) = \theta_0 \quad \forall t
\]
Since the normal hydrodynamic forces depend on location and time $t$, erosion will occur for those points on the agglomerate surface that, at time $t$, are in an arc such that

$$\frac{5}{4} \mu \dot{\gamma}(t) \sin 2 \varphi - \sigma_z \geq 0 \quad \text{(for } \theta = \frac{\pi}{2}).$$

This condition, at any given time, defines an eroding arc. For example, in the case of a steady simple shear flow ($\dot{\gamma}$ constant in time), the eroding arc is shown in Fig. 4.6 for different values of the fragmentation number $F_a$ plotted in the radial direction. The eroding arc ranges from 0 to the limiting value of $\pi$ when $F_a$ becomes infinite. The fragmentation number $F_a$ in this case is defined as the ratio between a characteristic hydrodynamic stress and the cohesive strength.

Scurati [34] computed the likelihood of erosion and erosion history for different flow geometries and various fragmentation numbers. They found that oscillatory shear flow is more efficient than the steady shear flow, particularly at low fragmentation numbers.

The complex dependence of dispersion kinetics on hydrodynamic conditions can be illustrated using the results shown in Fig. 4.7. Two sets of dispersion results for precipitated silica particles are shown; one for low density (and hence weaker) agglomerates, and the other for higher density (stronger) agglomerates. The mean stress in all experiments was set to an identical value (580 Pa) by using either a lower viscosity PDMS fluid (10 Pa s) at a higher shear rate (red symbols) or a higher viscosity PDMS fluid (30 Pa s) at a lower shear rate (blue symbols). The magnitude of the dispersion rate is larger for the case of the lower density agglomerates. However, note that dispersion proceeds at a faster rate for the cases when a higher shear rate was applied than when using a lower shear rate. This suggests that characterization of the hydrodynamic conditions through shear stress alone is not adequate for the prediction of dispersion kinetics. Furthermore, the ratio of shear stress to cohesivity is not sufficient for the prediction of dispersion kinetics.
Based on analysis of a wide range of experimental observations, a useful form for a more comprehensive kinetic model is [35]:

\[
\frac{dR}{dt} = K \left( F_h - F_c \right) \frac{\dot{\gamma}}{2} \quad \text{for } F_h > F_c
\]  

(4.23)

where \( R \) is the radius of the agglomerate, \( F_h \) is the hydrodynamic force applied to the agglomerate, \( F_c \) is the cohesivity of the agglomerate, \( \dot{\gamma} \) is the shear rate, and \( K \) is a scaling parameter that reflects the geometry of the flow field. The left-hand side of this expression characterizes the rate of material removal from the parent agglomerate. Unless the hydrodynamic force exceeds the agglomerate cohesivity, no dispersion will take place. The dispersion rate is taken to be proportional to the hydrodynamic force applied in excess of the cohesive force (which determines whether fragments can be broken from the parent agglomerate) and the applied shear rate (which determines the rate at which fragments can be removed from the vicinity of the parent agglomerate). The model expressed in Eq. (4.23) can be rewritten in terms of strain by recognizing that \( \dot{\gamma} = \dot{\gamma} t \) as

\[
\frac{\delta R}{\delta \gamma} = K \left( F_h - F_c \right) \frac{1}{2}
\]  

(4.24)
Figure 4.7: Dispersion kinetics for precipitated silica agglomerates. The upper graph shows results for the case of low density \( \phi/(1-\phi) = 0.184 \) agglomerates, while the graph on the bottom shows results for higher density \( \phi/(1-\phi) = 0.191 \) agglomerates.
4.2 Continuum Dispersion Models

Figure 4.8 shows the dispersion results of Fig. 4.7 plotted according to strain as per Eq. (4.24). All of the data collapse to a single curve, providing additional evidence for the appropriateness of the relationships provided in Eq. (4.23).

Another test for the kinetic model given by Eq. (4.23) can be performed by analyzing dispersion under conditions involving fixed power input to the fluid, but wherein fluids with different viscosity are used. If the hydrodynamic force applied is much larger than the maximum cohesive force of the agglomerate ($F_h > F_c$), the erosion rate becomes proportional to the energy input of the system:

$$-\frac{dR}{dt} \propto (F_h - F_c) \frac{\dot{\gamma}}{2} \equiv \mu \frac{\dot{\gamma}^2}{2} \equiv \frac{P}{V}$$

However, for smaller hydrodynamic force ($F_h \approx F_c$), this proportionality is lost. Experimental results confirmed the predictions.

In Figs. 4.9 and 4.10, we present the erosion kinetics observed when dispersing identical silica agglomerates ($\phi/(1 - \phi) = 0.194$) using fluids of different viscosity to give an energy input per unit volume of 50,000 or 90,000 W/m$^3$. In the case of the lower energy input (Fig. 4.9), faster erosion kinetics is observed due to the higher hydrodynamic stress applied. However the erosion kinetics becomes proportional to the power input at higher stress (see Fig. 4.10). These results are consistent with model predictions.
Erosion Kinetics for Identical Power Input
$P/V = 50.000 \text{ W/m}^3$, $\phi/(1-\phi) = 0.194$

- Model Prediction $\eta=10 \text{ Pa s}$
- Model Prediction $\eta=10 \text{ Pa s}$
- Experiments $\eta=30 \text{ Pa s}$
- Experiments $\eta=30 \text{ Pa s}$

**Figure 4.9:** Dispersion results at fixed power input, but with the applied stress comparable to the cohesive strength of the agglomerate

Erosion Kinetics for Identical Power Input
$P/V = 90.000 \text{ W/m}^3$, $\phi/(1-\phi) = 0.194$

- Model Prediction $\eta=10 \text{ Pa s}$
- Model Prediction $\eta=10 \text{ Pa s}$
- Experiments $\eta=30 \text{ Pa s}$
- Experiments $\eta=30 \text{ Pa s}$

**Figure 4.10:** Dispersion results at fixed power input, but with the applied stress far in excess of the cohesive strength of the agglomerate
4.3 Discrete Dispersion Models

Accessibility to more powerful computers has rendered intensive numerical approaches more amenable to the study of dispersion, in its complexity. The study of particulate assemblies using the discrete element method, developed by Cundall and Strack [36] in the late 1970s, has been applied by such researchers as Thornton et al. [37] to develop three-dimensional simulations of agglomerate break-up upon impact, and Tsuji et al. [38] to study the convection of spherical particles along horizontal pipes. Higashitani et al. [39] adopted the approach to create a three-dimensional model of agglomerate dispersion in response to steady shearing. In their analysis, they calculated a hydrodynamic force acting on the external surface of each individual particle of the agglomerate as if it were embedded in a fluid flowing at a uniform velocity, modified to account for the presence of neighboring particles. Interaction forces between the comprising particles were assumed to include an attractive van der Waals force term and a Voigt model term to account for volume exclusion effects. Moribe and White [40] followed the same general approach, using Stoke's law to find the hydrodynamic force acting on each particle. Gopalkrishnan et al. [41] applied DEM to a simplified representative agglomerate model to probe adhesive and cohesive failure modes in partially infiltrated agglomerates.

Fanelli, Feke and Manas-Zloczower [42, 43] adopted the discrete/distinct element method to solve the force balances about the individual clusters which comprise the agglomerate:

\[
m \ddot{x}_i = \sum_{\text{exposed surface areas}} \vec{F}_{hi} + \sum_{\text{neighboring clusters}} \vec{F}_{cij} + \vec{F}_{dij}
\]

where

- \(m\) = mass of the cluster,
- \(\ddot{x}_i\) = acceleration of the individual cluster relative to the agglomerate,
- \(\vec{F}_i\) = net force acting on the individual cluster within an agglomerate,
- \(\vec{F}_{hi}\) = hydrodynamic force acting on the individual cluster through part of its exposed surface area,
- \(\vec{F}_{cij}\) = cohesive force acting on the individual cluster because of its interaction with another, neighboring cluster,
- \(\vec{F}_{dij}\) = drag force exerted on the individual cluster by the surrounding fluid.

All calculations were performed with nondimensionalized force balances, to facilitate comparisons and allow better understanding of parameter effects. The force balance equations are integrated, using the velocity verlet explicit algorithm, to give cluster positions as a function of time with a local error of order \(\Delta t^4\) [44], where \(\Delta t^*\) is the dimensionless time step for the calculation. The program code was written in Matlab.

The agglomerate was defined as an ordered system of individual clusters (organized in simple cubic or body centered cubic configurations) or as a random assembly of clusters (created by
generating randomly distributed cluster center points about an origin (0, 0, 0) and pulling them radially inward, beginning with the innermost cluster, until they come within a pre-defined distance of each other). Random cluster configurations generated in this manner lead to fractal agglomerates. The cluster placed at the core of the agglomerate was held at the origin throughout the run. Connectivity to this central cluster (through any branching of interacting, neighboring clusters) determines whether any other cluster is attached to the agglomerate. The radius of the agglomerate was updated continuously, and taken to be half of the maximum distance between any two clusters within the agglomerate. All clusters were assumed to have equivalent radii and density.

The hydrodynamic force exerted on each cluster was calculated by finding the hydrodynamic force exerted on small external surface sections, or caps, of the agglomerate (assumed to be an impermeable sphere for the calculation), and distributing this force to all exposed clusters underneath the surface sections. Hence, only those clusters that are exposed to the exterior surface experience a hydrodynamic force.

The force transmitted to the agglomerate surface by the simple shear flow field is expressed below, in spherical coordinates, in terms of cap size and position on the agglomerate

$$\tilde{F}_{hk} = \frac{5}{2} \mu \pi R^2 \sin^2 \xi_o \gamma \begin{bmatrix} \sin^2 \theta_o \sin 2\phi_o \\ \sin \theta_o \cos \theta_o \sin 2\phi_o \\ \sin \theta_o \cos 2\phi_o \end{bmatrix}$$

where

- $\tilde{F}_{hk}$ = hydrodynamic force transmitted to the surface section of an agglomerate cap, $k$,
- $\mu$ = dynamic viscosity of the dispersing fluid,
- $R$ = radius of the agglomerate,
- $\xi_o$ = polar angle defining the size of the agglomerate cap,
- $\theta_o$ = polar angle defining the position of the cap on the agglomerate,
- $\phi_o$ = azimuthal angle defining the position of the cap on the agglomerate,
- $\gamma$ = shear rate of the flowing fluid.

The cohesive force between clusters was modeled as the summation of van der Waals attractive and Born repulsive forces, calculated by differentiating available expressions for unhindered inter-cluster potentials [45,46].

$$\tilde{F}_{ij} = \sum_{\text{contact points}} \tilde{F}_{ij} \text{Born} + \tilde{F}_{ij} \text{van der Waals}$$

$$\tilde{F}_{ij} \text{van der Waals} = \frac{A}{a} \left[ \frac{32}{3 |r_{ij}|^3 (|r_{ij}|^2 - 4)^2} \right]$$
4.3 Discrete Dispersion Models

where

\( \tilde{F}_{ij} \) = van der Waals inter-cluster attractive force,

\( \tilde{F}_{ij} \) = Born inter-cluster repulsive force,

\( A \) = Hamaker constant for the cluster material,

\( a \) = radius of the clusters,

\( \sigma \) = separation distance at which the inter-atomic potential of the cluster material is zero,

\( |\tilde{r}_{ij}| \) = distance between interacting cluster center points, normalized with respect to the cluster radius.

The drag force acting on each cluster was defined by applying Stokes’s law to each cluster as if it were flowing at steady state in an infinite fluid under creeping flow conditions [47]. Thus, each cluster was assumed to be fully surrounded by the dispersing fluid, and

\[
\tilde{F}_{ii} = 6 \pi \mu \frac{a}{\sigma} \left( \tilde{v}_{ik} - \tilde{x}_i \right)
\]  

where

\( \tilde{v}_{ik} \) = velocity of the fluid, calculated at the individual cluster center point [48],

\( \tilde{x}_i \) = velocity of the individual cluster.

To obtain relatively fast turn-around times (involving several weeks of computation on the Ohio Super Computer’s SUN SunFire 6800 and Pentium 4 Cluster systems), the authors considered agglomerates limited to a small number of comprising clusters, with uniform material properties and dimensions.

To gauge the effect of scale transition from macro- to nano-scales on dispersion processing requirements, the authors conducted a brief analysis using four regular agglomerates with the same body centered cubic cluster configuration. As shown in Fig. 4.11, all agglomerates consisted of 259 clusters, with the same agglomerate to cluster radius ratio, \( R/a = 8.2 \), and porosity, 0.53. The following material parameters, representative of silica, were fixed for all cases:
The agglomerates were oriented in a steady flow field so that the outermost cluster was at the most stressful point on the agglomerate. The minimum hydrodynamic stress required to pull this exterior cluster from the agglomerate (to overcome the maximum attractive force of interaction between two clusters) was calculated and termed the critical stress for dispersion. As the results summarized in Table 4.1 and Fig. 4.12 indicate, for the same agglomerate to cluster radius ratio, the critical stress for dispersion is inversely proportional to the cluster size. The dependence is significant and emphasizes that dispersion on the nano- and micro-scales requires much greater stresses than dispersion on the macro-scale.

Table 4.1: Effect of cluster size on ease of dispersion of the regular, body centered cubic, 259-cluster agglomerate. The maximum force of attraction between clusters increases and the critical stress for dispersion decreases as cluster size increases.

<table>
<thead>
<tr>
<th>(a) (nm)</th>
<th>Maximum force of interaction between clusters (N)</th>
<th>Critical stress for dispersion (Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>(6.3 \cdot 10^{-11})</td>
<td>320,330</td>
</tr>
<tr>
<td>40</td>
<td>(7.95 \cdot 10^{-10})</td>
<td>43,720</td>
</tr>
<tr>
<td>400</td>
<td>(8.13 \cdot 10^{-9})</td>
<td>4,470</td>
</tr>
<tr>
<td>4,000</td>
<td>(8.15 \cdot 10^{-8})</td>
<td>500</td>
</tr>
</tbody>
</table>

Figure 4.11: Three- and two-dimensional views of a body centered cubic, regular agglomerate cluster configuration, specific to an agglomerate with 4 nm cluster radii. Cluster radii are not to scale.
4.4 Dispersion Mechanisms and Modelling Based on Experimental Observations

Experimental observations on dispersion phenomena for model systems in well-defined flow fields constitute the basis for some simple mathematical models also reported in the literature. Powell and Mason [49] studied the dispersion of cohesionless clusters of spherical particles in laminar flow fields. The clusters were obtained by suspending solid spherical particles (20–400 μm) in high viscosity silicone oils at large volume fractions (0.6). Dispersion phenomena were studied in well-defined laminar flows (simple shear and pure elongation) of the same silicone fluid. The results obtained were interpreted in terms of a simple model proposed initially by Kao and Mason [15]. This model assumes that the rate at which particles leave the surface of the cluster is proportional to the surface area of the cluster, which can be formulated as follows:
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\[ \frac{dN}{dt} \propto \left( \frac{R}{a} \right)^2 \quad (4.32) \]

where \( N = N(t) \) is the surface-average number of particles that have detached from the cluster since the initiation of an experiment until time \( t \), \( R \) is the agglomerate radius, and \( a \) is the radius of individual spheres forming the cluster. Since \( (a^3) \frac{dN R^2}{dt} \) is proportional to the rate of decrease of the cluster volume, Eq. (4.32) can be written:

\[ \frac{d(R/R_0)}{dt} = -\hat{k} \frac{a}{R_0} \quad (4.33) \]

Here, \( \hat{k} \) is the proportionality constant, which depends on the local velocity gradient, the volume fraction of particles in the cluster, and the geometry of the flow field. The authors found that this proportionality constant was significantly influenced by the flow geometry, with the elongational flows enhancing the dispersion process. Also, the rate of dispersion was strongly dependent on the ratio of the particle radius to the initial cluster radius.

Shiga and Furuta [50] proposed the “onion model” based on experimental observations of carbon black dispersion in rubber compounds. According to this model, aggregates are either individually or collectively scraped from the surface of the agglomerate. The authors developed a model to calculate particle size distribution functions based on the assumption that each pass of an agglomerate through a high shear zone region will reduce its weight by a quantity, \( \Delta M \), proportional to the hydrodynamic stress exerted on the surface of the agglomerate \( \sigma \), the agglomerate size \( R \), and the residence time \( t \) in the high shear field:

\[ -\Delta M \propto \sigma R^2 t \quad (4.34) \]

The model developed based on Eq. (4.34) seems to describe at least semi-quantitatively the changes in agglomerate size distribution with mixing time.

Rwei, Manas-Zloczower, and Feke [51, 52] observed two distinct mechanisms of dispersion in their experiments of carbon black agglomerate breakup in a transparent cone-and-plane device. One mechanism, called “erosion”, initiates at lower shear stresses and is characterized by a continuous detachment of small fragments from the outer shell of the pellet. The other mechanism, called “rupture”, was characterized by an abrupt splitting of the agglomerate into a small number of large fragments and occurs at relatively higher shear stresses.

For the erosion process, following Powell and Mason’s lead (Eqs. (4.32) and (4.33)), Rwei et al. [52] expressed the rate at which particles erode from a cluster as follows:

\[ \frac{dR}{dt^*} = -k_1 \langle a \rangle \quad (4.35) \]

where \( R \) is the cluster radius, \( \langle a \rangle \) is volume-average radius of the fragments, \( k_1 \) is the rate constant, and \( t^* = \frac{t}{\dot{y}} \) is a dimensionless erosion time (\( \dot{y} \) is the shear rate in the flow field).

Assuming, based on experimental observations, the size of the eroded fragments to be proportional to the size of the parent cluster, \( \langle a \rangle = b R \), where \( b \) is a constant, leads to
4.4 Dispersion Mechanisms and Modelling Based on Experimental Observations

\[
\ln \frac{R(t)}{R_0} = b \ k_1 \ t^* = \lambda \ t^*
\]  (4.36)

For short erosion times, Eq. (4.36) can be written:

\[
\frac{R_0 - R(t)}{R_0} = \lambda \ t^*
\]  (4.37)

The rate constant \( \lambda \) is believed to depend on the flow geometry, the applied shear stress, and the cohesive strength of the agglomerate. Figure 4.13 shows the experimental data for the fractional change in agglomerate size as a function of the dimensionless shearing time. These data fit well the functional forms predicted by Eqs. (4.36) and (4.37).

The size analysis of fragments produced by erosion showed a Gaussian distribution function. At higher applied shear stresses, when rupture occurs, a broad log-normal distribution was found, typical for dispersions produced by comminution. For different levels of applied shear stress, the mean value and standard deviation of the particle volume distribution curves were observed to shift. A parameter scaling the applied shear stress with the cohesive strength of the agglomerates was found to be characteristic for both the erosion and the rupture processes.

Yamada, Manas-Zloczower, and Feke [53, 54] investigated the effect of agglomerate permeability and matrix infiltration on the dispersion mechanisms and kinetics in the case of carbon black agglomerates subjected to simple shear flow in polydimethyl siloxane fluids. The authors identified two characteristic length scales that affect the dispersion process. One length scale (\( L_p \)) is a measure of the ease with which fluid can flow through the porous agglomerate structure, where \( L_p = k^{1/2} \) (\( k \) is agglomerate permeability) and is directly related to its packing density and the morphology of the constituent particles. The second parameter, \( \delta \), is a measure of the depth to which processing fluid has soaked into the agglomerate.

![Figure 4.13: Extent of erosion as a function of dimensionless time, showing linear behavior for short times and exponential behavior at long times](image)
due to surface tension effects. Evaluation of the parameters $L_p$ and $\delta$ was inferred from the hydrodynamic drag coefficient exhibited in sedimentation or flotation experiments. Values of $L_p$ were found to be relatively large for high structure carbon blacks and low density agglomerates. The parameter $\delta$ varies with time of immersion in the processing fluid.

Different dispersion behavior may be expected depending on the value of $\delta$ relative to $L_p$. When $\delta < L_p$, all of the fluid present within the agglomerate can respond to the external flow field, and hydrodynamic stresses may directly bear upon the interface between the dry and soaked portions of the agglomerate. Relatively fast dispersion and $\delta$-sized fragments might be expected. However, as infiltration proceeds, $\delta$ may eventually exceed $L_p$. In this case, there is significant hydrodynamic resistance to flow for the fluid located near the interface between the dry and soaked portions of the agglomerate. Correspondingly, there will be less hydrodynamic stress acting on this interface, and a different dispersion mechanism may be expected. The two different erosion regimes are schematically depicted in Fig. 4.14.

Erosion kinetic results for two different grades of carbon black (high and low structure) are presented in Figs. 4.15 and 4.16. The kinetics of erosion was analyzed in terms of the fractional reduction in parent size ($1 - R/R_0$, where $R_0$ is the initial size of the agglomerate) as a function of shearing time. The results indicate a drastic change in the kinetics of erosion at an agglomerate density of around 0.345 g/cm$^3$. Agglomerates with densities lower than this value exhibit persistent high erosion rates which show a nearly linear dependence on the reduction of the parent agglomerate with shearing time. For agglomerates with densities above this critical value, the erosion kinetic curves show a plateau value after shearing times on the order of ten minutes. These results correlate well with the evolution of the $\delta/L_p$ ratio as a function of shearing time. Figures 4.17 and 4.18 plot the ratio of $\delta'/L_p$ as a function of shearing time for the various agglomerates studied (here $\delta'$ represents an effective depth to which the fluid has infiltrated into an eroding agglomerate). The results shown in Figs. 4.17 and 4.18 indicate a critical ratio of $\delta'/L_p = 2.5$. When $\delta'/L_p$ is below 2.5, fast erosion occurs, and when $\delta'/L_p$ exceeds 2.5, slow erosion occurs. Note that $L_p$ is only a characteristic length and that the actual depth to which fluid can flow within the agglomerate can be a multiple of $L_p$.
4.4 Dispersion Mechanisms and Modelling Based on Experimental Observations

Figure 4.15: Erosion kinetic curves for agglomerates of the high structure carbon black sheared at 56.7 s\(^{-1}\) in PDMS of 30,000 cS viscosity

Figure 4.16: Erosion kinetic curves for agglomerates of the low structure carbon black sheared at 56.7 s\(^{-1}\) in PDMS of 30,000 cS viscosity

Figure 4.17: Evolution of $\delta'/L_p$ ratio with time of shearing for agglomerates of the high structure carbon black sheared at 56.7 s\(^{-1}\) in PDMS of 30,000 cS viscosity

Figure 4.18: Evolution of $\delta'/L_p$ ratio with time of shearing for agglomerates of the low structure carbon black sheared at 56.7 s\(^{-1}\) in PDMS of 30,000 cS viscosity.
Lee, Feke, and Manas-Zloczower [55] examined the dispersion behavior of titanium dioxide in viscous media and found that the kinetics of the erosion process was highly sensitive to the overall porosity of the agglomerates. In the case of high porosity agglomerates, the erosion rate is highly affected by the speed of medium penetration into the agglomerate and the eroded fragments exhibit a broad size distribution. By contrast, low porosity agglomerates erode by the detachment of small, relatively uniform size fragments from the outer surface of the agglomerate. Figure 4.19 compares the rates of matrix infiltration and agglomerate erosion for various porosity clusters. Infiltration rates for powder compacts having porosity of less than 0.72 were small and could not be reliably measured. The abrupt break in the erosion rate constant at 0.65 agglomerate porosity is related to a significant shift in the extent of medium infiltration within the powder compact. For agglomerates with porosities exceeding this critical value, the erosion rate parallels the dependence of the rate of matrix infiltration on porosity. The size of eroded fragments illustrated in Fig. 4.20 correlates well with the porosity of the parent agglomerate.

Another potential consequence of fluid infiltration is illustrated in Fig. 4.21. For some types of agglomerates, the infiltration process can actually reduce the magnitude of the stress necessary to induce dispersion in comparison to that required for a dry agglomerate. If the capillary force associated with the wetting of the agglomerate by the processing fluid exceeds the cohesive forces binding the agglomerate together, then the force that acts to draw the processing fluid into the agglomerate also pulls the particles within the periphery of the agglomerate away from its core. Thus, the interface between the wet periphery and dry core of the agglomerate is weakened. In such cases, the application of hydrodynamic shear can peel away the wetted peripheral region from the dry agglomerate core.

In some of our work involving the dispersion of fumed silica agglomerates in silicone oil we have found that dispersion can be initiated at applied stresses substantially below the strength of the fully infiltrated agglomerate and that the fragments produced have a thickness that is comparable to the depth of fluid that infiltrates prior to the application of shear [56].

Figure 4.19: Comparison of erosion and matrix infiltration rate for titanium dioxide agglomerates
4.4 Dispersion Mechanisms and Modelling Based on Experimental Observations

**Figure 4.20:** Photographs of eroded fragments from titanium dioxide agglomerates at the initial stage of shearing (a) 0.696 porosity; (b) 0.645 porosity; (c) 0.574 porosity; (d) 0.499 porosity

**Figure 4.21:** Schematic representation of the formation of a structural discontinuity within an agglomerate at the wet-dry interface due to capillary pressure driven infiltration. Such a weakened interface leads to another mechanism of agglomerate dispersion known as adhesive failure.
4.5 Concluding Remarks

The dispersion of solid agglomerates in liquid media is governed by a number of competing chemical and physical effects, related to both the nature of the agglomerates themselves and the processing conditions under which the dispersion takes place. Despite these complexities, there has been considerable advances in the sophistication and usefulness of modeling of the relevant phenomena. In general, two distinct breakage mechanisms have been observed in agglomerate dispersion processes: a large-scale fragmentation process denoted as rupture and a fine-particle erosion. The critical conditions for the onset of dispersion as well as the process outcome depend on the structure and cohesivity of the solid agglomerates, the strength and geometry of the applied flow field, and the energetics of the agglomerate-medium interaction.

Erosion is the process of continuous detachment of particles and/or small fragments from the outer surface of the agglomerate. For cohesive agglomerates, the kinetics of the process depends on the strength of the applied flow field. By contrast, for cohesionless agglomerates, the kinetic rate constant is independent of the flow strength. Erosion is initiated at lower applied shear stresses than rupture. Matrix penetration in the outer regions at the agglomerate boundary is believed to lower the strength of attachment of potential fragments near the surface and facilitate their breakup.

Rupture is an abrupt, large-scale fragmentation process. Rupture is initiated at higher applied shear stresses than erosion and produces a broad log-normal size distribution of fragments [51]. Typically, rupture occurs at applied shear stresses lower than the ones predicted from agglomerate cohesivity measurements. The presence of structural heterogeneities in agglomerates may provide an explanation for this discrepancy [23].

In cases where the magnitude of particle-fluid capillary forces exceed the cohesivity of the agglomerate, a third type of dispersion mechanism can occur. In this case, the infiltration of processing liquid into the agglomerate can drive structural rearrangement which may lead to adhesive failure of the wetted portions of the agglomerate from dry portions. This type of failure can occur at applied stresses substantially lower than might be expected on the basis of measurements of cohesivity performed for dry agglomerates.

Most of the models of agglomerate breakup presented above generally do not address the issue of structural heterogeneities within the cluster. Such heterogeneities are of extreme significance in the dispersion process, since they correspond to weak portions of the agglomerate (where the agglomerate might first fall), as well as to strong portions of the agglomerate (which resist dispersion). Detailed modeling approaches, such as the DEM method described earlier, can be applied to agglomerates with precisely defined packing structures, whether they be regular or random. Information useful to understanding the dispersion of real agglomerates can be derived from these models.

Finally, there have been several advances in the development of phenomenological models for the dispersion process. It is clear that the geometry of the flow field in which dispersion takes place greatly influences the kinetics and the outcome of the process. For example, experimental results [15, 49] and theoretical predictions [33] point out that elongational flow enhances the process of agglomerate dispersion.
The applicability of various dispersion models for predictive studies in mixing operations depends primarily on the information available on various system (material and processing) parameters. However, such models are important, because they provide the theoretical framework within which further investigations of the dispersion process may be conducted.

**Nomenclature**

\( \langle a \rangle \) Volume average size of fragment  
\( a \) Aggregate radius  
\( A \) Mobility function (Eq. (4.7))  
\( A \) Hamaker constant (Eq. (4.30))  
\( B \) Mobility function (Eq. (4.7))  
\( b \) Ratio of fragment size to agglomerate size  
\( c \) Mean coordination number  
\( d \) Particle diameter  
\( D \) Agglomerate/fragment size  
\( D_f \) Fractal dimension  
\( E \) Rate of deformation tensor  
\( E \) Local rate of erosion (Eq. (4.14))  
\( F \) Mean interparticle force within agglomerate (Eq. (4.1))  
\( f_a \) Fragmentation number (Eq. (4.13))  
\( F \) Fraction of agglomerates broken (Eq. (4.9))  
\( F_a \) Fragmentation number (ratio of characteristic hydrodynamic stress and cohesive strength)  
\( F_{pp} \) Interparticle force per unit fraction area  
\( F_i \) Net force acting on an element within a cluster  
\( F_c \) Cohesive force  
\( F_{di} \) Drag force exerted on element \( i \) within a cluster  
\( F_{cij} \) Cohesive force acting between elements \( i \) and \( j \) within a cluster  
\( F_h \) Hydrodynamic force  
\( F_{hij} \) Hydrodynamic force acting on a portion of a cluster  
\( F_{y, \text{Born}} \) Born force between elements \( i \) and \( j \) of a cluster  
\( F_{y, \text{van der Waals}} \) van der Waals force between elements \( i \) and \( j \) of a cluster  
\( H^0 \) Effective surface separation distance at zero tensile strength
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Scalars in Eq. (4.6)

Identity tensor

Number of agglomerate consecutive breakings

Agglomerate permeability

Proportionality constant (Eq. (4.23))

Erosion rate constant (Eq. (4.35))

Proportionality constant (Eq. (4.33))

Bulk modulus

Likelihood of erosion (Eq. (4.12))

Length scale for fluid flow inside a porous agglomerate

Elastic shear modulus

Mass of cluster

Agglomerate mass

Unit vector describing orientation

Number of particles detached from a cluster

Maximum number of breakings for an agglomerate

Pressure

Power

Position vector

Distance between elements $i$ and $j$ within a cluster, normalized by the cluster radius

Agglomerate radius, radius of sphere in a doublet (Eq. (4.6))

Surface average number of particles detaching from agglomerate

Number of bonds to be severed simultaneously for agglomerate rupture

Particle surface area

Apparent separation distance between particle surfaces

Time

Dimensionless time

Apparent separation distance between particles at zero tensile strength

Agglomerate tensile strength

Fluid velocity

Solid velocity

Local energy of distortion

Critical energy for agglomerate rupture

Particle volume
Nomenclature

\( \mathbf{v} \) \hspace{1cm} Velocity vector
\( V \) \hspace{1cm} Mixer/system volume
\( \mathbf{\tilde{v}}_i \) \hspace{1cm} Velocity vector for the fluid near element \( i \) within a cluster
\( W_i \) \hspace{1cm} Fraction of \( i \)-sized agglomerates (Eq. (4.9))
\( \mathbf{\dot{x}}_i \) \hspace{1cm} Acceleration vector of element \( i \) within a cluster
\( \mathbf{\tilde{x}}_i \) \hspace{1cm} Velocity vector for element \( i \) within an cluster
\( Y_i \) \hspace{1cm} Volume fraction of \( i \)-sized fragments in the system (Eq. (4.10))
\( Z \) \hspace{1cm} Ratio of hydrodynamic to cohesive forces (Eq. (4.8))
\( \alpha \) \hspace{1cm} Length of flaw within agglomerate
\( \varepsilon \) \hspace{1cm} Agglomerate porosity
\( \rho \) \hspace{1cm} Agglomerate density
\( \rho_s \) \hspace{1cm} Particle density
\( \sigma \) \hspace{1cm} Stress tensor
\( \sigma_{10} \) \hspace{1cm} Deviatoric part of stress tensor
\( \sigma \) \hspace{1cm} Separation distance at which the interatomic potential is zero
\( \dot{\gamma} \) \hspace{1cm} Shear rate
\( \Gamma \) \hspace{1cm} Interfacial energy between elastic spheres
\( \Gamma_c \) \hspace{1cm} Fracture energy
\( \delta \) \hspace{1cm} Length scale for fluid penetration
\( \mu \) \hspace{1cm} Fluid viscosity
\( \tau \) \hspace{1cm} Fluid stress tensor
\( \tau \) \hspace{1cm} Period of rotation
\( \dot{\gamma} \) \hspace{1cm} Applied shear rate
\( \lambda \) \hspace{1cm} Erosion rate constant (Eq. (4.36))
\( \Lambda \) \hspace{1cm} Size ratio of touching spheres in a doublet
\( \omega \) \hspace{1cm} Vorticity vector
\( \theta, \theta_0 \) \hspace{1cm} Polar angle, polar angle of the normal to a fracture surface
\( \varphi, \varphi_0 \) \hspace{1cm} Azimuthal angle, azimuthal angle of the normal to a fracture surface
\( \phi \) \hspace{1cm} Volume fraction of solids within a cluster
\( \psi \) \hspace{1cm} Polar angle
\( \xi \) \hspace{1cm} Azimuthal angle
\( \chi \) \hspace{1cm} Scalar reflecting the geometry of the breakup process (Eq. (4.8))
References