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Fragmentation and restructuring of soft-agglomerates under shear

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ABSTRACT

Soft-agglomerate restructuring, break-up (or fragmentation) and relaxation are studied in a simple shear flow by a discrete element method (DEM). The agglomerates, held together by van der Waals forces, rotate in the shear flow and are stretched into nearly linear structures (fractal dimension approaches unity) until they fracture at their weakest point resulting in lognormally-shaped fragment size distributions asymptotically. Individual fragments relax in the flow towards more compact agglomerates than the parent ones. The evolution of the average number of particles per fragment is described by generalized scaling laws between shear rate, onset (time-lag) of fragmentation, asymptotic fragment mass and size consistent with experimental and theoretical studies in the literature. The initial effective fractal dimension of the agglomerates influences the final one of the fragments.

1. Introduction

The dispersion of solid particles, such as inorganic nanoparticles or polymer latexes, in a fluid is an important process for commercial products containing particulate materials, like pigments, chemical–mechanical polishing agents or cosmetics. Population balance equations (PBE) are commonly used to model large particle systems using appropriate kernels for coagulation and breakage [1]. Shear-induced coagulation alone leads to gelation [2]. However in aerosol flow reactors, fluid flow promotes restructuring and fragmentation, which delays or prevents gelation [3]. Though coagulation by Brownian and shear forces seems to be reasonably well understood [1], fragmentation rates and size distributions are typically based on different assumptions [4]: namely instantaneous break-up of agglomerates once the hydrodynamic stress reaches a critical value [5], empirical breakage distribution functions [6–8] and a power law for the average fragment mass [5,9]. Moreover, fragments are more compact than their parent agglomerate after break-up in constant shear [5,10–12] but the mechanism of fragment relaxation is still subject of current research. Power law relationships were found in various experimental [5,13] and numerical studies [9,14]. The time-lag for the onset of breakage and the fragment size distribution functions, however, are both difficult to study experimentally and are not yet understood. Blaser [15] applied digital image analysis to determine the deformation and breakage of flocs in shear flows, from which it can be concluded that break-up happens fast or even instantaneously [16] for brittle polymeric aggregates. Harada et al. [17] simulated restructuring of dense clusters and suggested a relationship of the long-term structural change to the fatigue crack growth of solid materials that takes a long time.

The present work investigates the restructuring, break-up and relaxation of soft-agglomerates held together by van der Waals forces using DEM simulations. The time-lag for fragmentation and the evolution of fragment mass are extracted from simulations and a scaling law is obtained which is supported analytically. Finally restructuring during and after break-up is discussed using the evolution of the average effective fractal dimension, $D_{f,F}$, of the fragments.

2. Theory

Agglomerates are formed by cluster–cluster agglomeration [18], an important growth mechanism e.g. in flame synthesis of materials [19], flocculation, and many natural systems [20]. These agglomerates are exposed to a shear flow and experience a drag force, determined for each particle with the free-draining approximation [21]. The shear stress is defined as the product of fluid viscosity, η_f, and shear rate, G. Here, the flow field is defined as a simple shear flow with a velocity gradient in y-direction. The simulation starts with a fully developed shear profile. This is the case, for example, in flame aerosol reactors in manufacture of fumed SiO_2 [3] and TiO_2 [22]. There agglomerates are formed by

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Nomenclature

A	Hamaker constant, J
D_f	fractal dimension
d	diameter, m
E	Young's modulus, N m^{-2}
F	force, N
$\mathbf{F}$	force vector, N
G	shear gradient, s^{-1}
I	particle inertia, kg m^2
k	spring constant, N m^{-1}
k_B	Boltzmann constant, m^2 kg s^{-2} K^{-1}
$\mathbf{M}$	moment vector, N m
m	particle mass, kg
n	number of particles
$\mathbf{n}$	unit vector
R_g	radius of gyration, m
t	time, s
V	volume, m^3
v	velocity, m s^{-1}
$\mathbf{v}$	velocity vector, m s^{-1}
$\mathbf{x}$	particle position vector, m
x, y, z	coordinates, m

Greek letters

γ	damping coefficient, kg s^{-1}
δ	particle surface to surface distance, m
η	dynamic fluid viscosity, Pa s
μ	friction coefficient
ρ	particle density, kg m^{-3}
φ_s	solid volume fraction
$\mathbf{\Omega}$	vorticity, s^{-1}
ω	angular velocity, s^{-1}

Subscripts

b	break-up
eff	effective
F	fragment
f	fluid
i, j	index of particle
max	maximum
min	minimum
n	number based average
P	parent
p	primary particle

Superscripts

$drag$	stokes drag force
$d_{\min}$	chemical dimension
k	positive integer
n	normal direction
q, r	scaling law exponents
t	tangential direction
vdW	van der Waals force
w, z	scaling law exponents

coagulation in highly turbulent (up to $Re = 10^6$) tubular flows [23] to large enough sizes that are then broken by shear-induced fragmentation [3]. Initially one agglomerate is placed at the center of a simulation cell (solid volume fraction $\varphi_s = 10^{-5}$) and the initial particle velocity is set according to flow velocity at the particle position. The trajectories are calculated from the force and torque balance on each particle. Lees–Edwards boundary conditions are applied [24]. When particles leave the simulation cell they reenter on the opposite side accounting for shear flow. The model permits restructuring as well as coagulation of the agglomerate fragments.

2.1. Agglomerate generation

Agglomerates are generated with a hierarchical cluster–cluster agglomeration algorithm in three dimensions [25]. To produce a cluster of $n_p = 2^k$ primary particles, initially $n^1 = n_p/2$ clusters consisting of two primary particles are generated independently by off-lattice random walk. In the next step, the two-particle clusters diffuse through the empty space to build $n^1/2$ four-particle clusters. This process is continued until one ramified cluster consisting of 2^k primary particles is obtained finally. The fractal dimension of the generated agglomerates is calculated with the density–density correlation function [26] and is 1.79 ± 0.03, consistent with Meakin [27], $D_f = 1.78$. The agglomerates are highly ramified and almost loopless.

2.2. Equations of motion

A discrete element method (DEM) is implemented to calculate the translational and rotational motion of each particle [28]. The particle position is obtained by integrating the force balance with a Verlet algorithm:

$$m_i \frac{d^2}{dt^2}\mathbf{x}_i = \sum \mathbf{F} = \sum_j \mathbf{F}_{i,j} + \mathbf{F}_i^{drag}, \tag{1}$$

where m_i is the particle mass, $\mathbf{x}_i$, the particle position vector, $\mathbf{F}_{i,j}$ are the inter-particle forces and $\mathbf{F}_i^{drag}$, the coupling force between particle i and the surrounding fluid. As the primary particles are spheres, the orientation is of no importance and the rotational velocity, ω_i, is calculated with the torque balance:

$$I_i \frac{d}{dt}\omega_i = \sum \mathbf{M} = \sum_j \mathbf{M}_{i,j} + \mathbf{M}_i^{drag}, \tag{2}$$

where $I_i = m_i d_i^2/10$ is the moment of inertia for a solid spherical particle with diameter d_i [29], $\mathbf{M}_{i,j}$ the inter-particle torques and $\mathbf{M}_i^{drag}$ is the hydrodynamic torque. Brownian motion of the particles is neglected as the agglomerate break-up is simulated at high Peclet numbers, where convection is dominant. The Peclet numbers, $Pe = 6\pi\eta_f(d/2)^3 G/k_B T$, in these simulations range from about 140 to 7000, where T is the temperature and k_B the Boltzmann constant. The applied force models and underlying assumptions are described below.

2.3. Inter-particle forces

Particles of 500 nm diameter in a simple shear flow are investigated. Corresponding to the DLVO theory [30], repulsive electrostatic and attractive van der Waals forces affect particles in aqueous solutions. For simplicity, more complex force models accounting for the retardation of van der Waals forces in liquids or electrostatic double layer repulsion are not included. The significant forces for the break-up process are the maximum attractive force and the hydrodynamic force [13]. Furthermore, gravity can be neglected for particles in this size range because the difference between particle and fluid density is very small.

The normal interaction forces between particles are separated in three regimes. For large distances, no force acts between particles. As particles approach each other, van der Waals forces start to attract the particles. The van der Waals force, F^{vdW}, is calculated by the simplified formula proposed by Hamaker [31]: