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Original Research Paper

Aggregation of nanoparticles in high ionic strength suspensions: Effect of Hamaker constant and particle concentration

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ABSTRACT

The kinetics of aggregation of nanocolloidal particles in suspensions has been studied using computer simulations based on Discrete Element Method. This study presents the analysis of the influence of Hamaker constant, Brownian forces and particle concentration on the aggregation time of nanoparticles in high ionic strength suspensions. Particle adhesion and cohesion were simulated using the van der Waals force equation. Half the particles were assigned a Hamaker constant of 9.0×10^{-20} J and the other half of the particles had the Hamaker constant varied from case to case with values between 1.0×10^{-20} and 9.0×10^{-20} J. Aggregation times obtained from analysing the number of interparticle contacts and number of singlets in the suspensions have been used to characterise the speed of the aggregation process. The simulation results show that when the strength of the van der Waals interaction increases the aggregation time decreases following a power law. In addition, the presence of Brownian forces speeds up the aggregation process. Finally, the relationship between packing fraction and aggregation times for singlets and contacts has been very well expressed by power laws.

1. Introduction

The control of long term stability of particulate dispersions is of crucial importance to a wide variety of industries including mineral processing and waste water treatment, and commodities such as paints, pharmaceuticals, and consumer care products. Whilst experimental methods are routinely utilised to assess suspension stability, the ability to simulate suspension behaviour computationally is becoming increasingly important. This is particularly true of samples that are costly (e.g. pharmaceuticals) or hazardous (e.g. biologically active particles), or to probe conditions for which there are not yet well-characterised model experimental analogues.

In the absence of steric stabilisation, polymer bridging, or strong solvent structural forces, the interaction energy between two colloidal particles can be expressed as the sum of attractive van der Waals force and the electric double layer repulsion according the well known Derjaguin–Landau–Verwey–Overbeek (DLVO) theory [1].

For two identical particles, the electrical double layer interaction energy, V_{edl} (J), as a function of separation distance between particle centres, r (m), is given by:

$$V_{edl} = 2\pi\varepsilon\varepsilon_0 R\psi_0^2 \exp(-\kappa r) \tag{1}$$

where ε is the dielectric constant of the intervening medium, ε_0 is the permittivity of free space (C V^{-1} m^{-1}), R is the particle radius (m), ψ_0 is the surface potential of the particles (V), and κ is the Debye constant (m^{-1}).

Furthermore, the electric double layer interaction is dependent on the electrolyte concentration through the Debye constant, κ, which may be calculated by:

$$\kappa = \left(\frac{2000 N_A e^2}{\varepsilon\varepsilon_0 k_B T}\right)^{1/2} \sqrt{I} \tag{2}$$

Here, N_A is the Avogadro number (mol^{-1}), e is the elementary charge on an electron (C), k_B is the Boltzmann constant (J K^{-1}), T is the temperature (K), and I is the solution ionic strength (mol L^{-1}). The ionic strength is the sum of all electrolyte concentrations and, where c_i and z_i are the concentration (mol L^{-1}) and charge of the ith electrolyte species, respectively, can be expressed as:

$$I = \frac{\sum_i c_i z_i^2}{2} \tag{3}$$

According to Eqs. (1) and (2), as the ionic strength increases, through electrolyte concentration or charge, so does the Debye constant. Consequently the exponential decay in the magnitude of the electrical double layer repulsion as a function of particle

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separation is more rapid. At electrolyte concentrations greater than 1 M one can think of the electrical double layer repulsion as being effectively “turned off”. This effect is important in industrial systems, such as minerals processing, where the level of dissolved salts can be quite high [2–4]. Under such conditions there is no barrier to particle–particle contact, unless other stabilisers such as steric polymer layers are employed, and materials will aggregate due to the presence of attractive van der Waals forces.

Ionic liquids are salts that have melting points below 100 °C; there is no solvent present, only the constituent cations and anions [5]. These liquids exhibit very unusual physico-chemical properties, whose quantification is the subject of extensive current research. A commonly studied protic ionic liquid is ethylammonium nitrate (EAN), which has an effective ionic strength of ~11 M. Thus the range of the electrical double layer repulsion between two charged surfaces in EAN is much shorter that the attractive van der Waals. A first approach to study these materials, and indeed any high ionic strength system, is to understand how the lack of electrical double layer repulsion affects particle aggregation.

Computer simulations based on Discrete Element Method (DEM) have only been used in the study of nanocolloidal suspensions in the last decade [6–11]. Most of these simulations include the influence of the electrical double layer for systems with initial solid concentrations ranging from 0.0084 to 0.40, and in general they deal with the aspects of aggregation and aggregate structures under different physico-chemical conditions. DEM provides an excellent way to understand the kinetics of aggregation of colloidal suspensions since the state of the system can be easily determined at any instance in time.

2. Discrete Element Method

Discrete Element Method (DEM) is a computer simulation methodology in which particles are assigned individual physical and mechanical properties. In DEM macroscopic properties are obtained from the microscopic behaviour of the particles. DEM was first developed for the study of rock mechanics [12] but has since been used for many particulate [13–15] and colloidal systems [6–11].

The motion of particles in DEM is determined by Newton’s second law, where the equations of motion are integrated numerically using a finite difference method [12] to determine the position of the particles at any time. More details about the DEM working procedure can be found elsewhere [13]. The forces acting on the particles can be decomposed into several components; contact, long range, Brownian and drag. Therefore, the general equation of motion can be written as:

$$m\frac{d^2\vec{x}}{dt^2} = \vec{F}_{cont} + \vec{F}_{lr} + \vec{F}_{brow} + \vec{F}_{drag} \tag{4}$$

where m is the mass of the particle (kg), $\vec{x}$ is the vector position of the particle (m), t the time (s), $\vec{F}$ the force (N) and the subscripts *cont*, *lr*, *brow* and *drag* referring to contact, long range, Brownian and drag, respectively. An equivalent equation for the angular coordinates is also used. No gravity has been considered in the simulations since particle weight is around 9 orders of magnitude smaller than the maximum value of the van der Waals force acting between two particles.

2.1. Contact forces

The only contact force considered in the simulations presented here is due to the elasticity of the particles. The elastic force experienced by two contacting particles is given by Hertz’ Law:

$$\vec{F}_{cont,n} = \frac{4}{3}E^* R^{*1/2}\delta_n^{3/2} \tag{5}$$

where δ_n (m) is the normal contact deformation and R^* (m) and E^* (Pa) are the reduced particle radius and elastic modulus, respectively, defined by:

$$\frac{1}{R^*} = \frac{1}{R_1} + \frac{1}{R_2}, \tag{6}$$

$$\frac{1}{E^*} = \frac{(1-\upsilon_1^2)}{E_1} + \frac{(1-\upsilon_2^2)}{E_2}, \tag{7}$$

where R_1 and R_2 are the particle radii, υ_1 and υ_2 are the Poisson’s ratios, of particles 1 and 2, respectively.

2.2. Long range forces

In this work, the long range forces that govern the attraction between particles are van der Waals forces. Electrostatic forces are a second long range force that have been considered in previous work [2], but are not included in these simulations since we are interested in the behaviour of particles in conditions where the electrical double layer is essentially zero. Such situations occur when mineral oxide particles are at their isoelectric point, when the concentration of dissolved electrolyte is extremely high, or when particles are dispersed in ionic liquids.

The van der Waals force is generally calculated from the equation given by Hamaker [16]:

$$\vec{F}_{\text{vdw}} = -\frac{HR^*}{6d^2} \tag{8}$$

where H is the Hamaker constant, d is the separation distance between particle surfaces and R^* is the reduced radius of two particles in contact. The Hamaker constant expresses the strength of the attractive interaction that naturally appears between different bodies due the interaction between microscopic dipoles.

Eq. (8) tends to infinity as d approaches zero, and so a minimum separation distance cut-off of 4 Å was assigned [17,18]. However, no maximum cut off distance has been considered in the simulations and therefore, every particle ‘feels’ the interaction of all the other particles.

2.3. Drag forces

The fluid in these simulations was assumed to be stationary. This assumption is reasonable as the particles are very small (100 nm) and the particle concentration is typically less than 5%. The Stokes’ drag force for a stationary fluid was used in these simulations, given by:

$$\vec{F}_{drag} = C_D\left(\frac{d\vec{x}}{dt}\right) \tag{9}$$

where the drag coefficient C_D is given by:

$$C_D = 6\pi R\mu \tag{10}$$

for a particle of radius R in a fluid with viscosity μ (Pa s).

2.4. Brownian forces

Brownian forces describe the random motion of particles in a fluid. The direction is randomly determined and the magnitude of the force follows a Gaussian, or normal distribution, with variance given by [19]:

$$\sigma^2 = \frac{6k_B T C_D}{\Delta t}, \tag{11}$$

where k_B is the Boltzmann constant, C_D the drag coefficient, T the absolute temperature and Δt the time step.