Supporting Information

"Aggregation and sedimentation of shattered graphene oxide nanoparticles (SGO) in dynamic environments: a solid-body rotational approach"

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Collision kernels. The collision kernel for environmental colloids is commonly given as the sum of three mechanisms including perikinetic collisions (Brownian), orthokinetic collisions (shear-induced aggregation when there is motion in the fluid), and differential settling which stands for collection of smaller aggregates by the larger ones in their sedimentation path.¹ Combining fractal dimension relationships and permeability drag effects^{2, 3} and expressing the collision rates with the solid volume (or mass) of aggregates as a representative variable,⁴⁻⁶ the following relationships yield:

$$\beta_{Prik}(i,j) = \frac{2k_b T}{3\mu} (v_i^{1/D_f} + v_j^{1/D_f}) (\frac{1}{\Omega_i} v_i^{-1/D_f} + \frac{1}{\Omega_j} v_j^{-1/D_f})$$
(S1)

$$\beta_{Orth}(i,j) = \frac{G}{\pi} v_0^{1-3/D_f} (\eta_{ci}^{1/2} v_i^{1/D_f} + \eta_{cj}^{1/2} v_j^{1/D_f})^3$$
(S2)

$$\beta_{Diff}(i,j) = \frac{3}{2} \left(\frac{\pi}{6}\right)^{1/3} v_0^{2/3 - 2/D_f} \left(\eta_{ci}^{1/2} v_i^{1/D_f} + \eta_{cj}^{1/2} v_j^{1/D_f}\right)^2 \left|U_i - U_j\right|$$
(S3)

The superposition of the three rates gives the total rate of collisions, $\beta(i,j)$:

$$\beta(i,j) = \beta_{Prik}(i,j) + \beta_{Orth}(i,j) + \beta_{Diff}(i,j)$$
(S4).

where β is the collision kernel or collision frequency $[L^{3}T^{-1}]$, β_{Diff} is the differential settling collision frequency $[L^{3}T^{-1}]$, β_{Orth} is the orthokinetic collision frequency $[L^{3}T^{-1}]$, β_{Prik} is the perikinetic collision frequency $[L^{3}T^{-1}]$, μ is the dynamic viscosity of the suspending medium [M $T^{-1}L^{-1}]$, *T* is temperature $[{}^{\circ}K]$, ${}^{k}{}_{b}$ is the Boltzman constant, ν is the solid volume of each aggregate $[L^{3}]$, ${}^{\nu}{}_{0}$ is the solid volume of primary particles $[L^{3}]$, *U* is the sedimentation velocity of each aggregate $[LT^{-1}]$, *G* is shear rate $[T^{-1}]$, ${}^{D}{}_{f}$ is fractal dimension [–], and Ω_{i} is the ratio of drag force exerted on a permeable aggregate to drag force exerted on an impervious aggregate with the same size, and can be calculated as for each aggregate in size class *i*:^{3, 7-9}

$$\Omega_{i} = \frac{2\xi_{i}^{2} \left(1 - \frac{\tanh(\xi_{i})}{\xi_{i}}\right)}{2\xi_{i}^{2} + 3\left(1 - \frac{\tanh(\xi_{i})}{\xi_{i}}\right)}$$
(S5)

where ξ_i is the non-dimensional permeability of the porous aggregates in each size class given as:

$$\xi_i = \frac{a_i}{\kappa_i^{1/2}} \tag{S6}$$

The fluid collection efficiency of each aggregate in size class *i*, η_{ci} , is defined as the ratio of flow through an aggregate to total flow approaching the aggregate and can be determined from the Brinkman equation:^{3, 10}

$$\eta_{ci} = 1 - \frac{d_c}{\xi_i} - \frac{c_c}{\xi_i^3}$$
(S7)

where

$$d_c = \frac{3}{J} \xi_i^3 \left(1 - \frac{\tanh\left(\xi_i\right)}{\xi_i} \right)$$
(S8)

$$c_{c} = -\frac{1}{J} \left(\xi_{i}^{5} + 6\xi_{i}^{3} - \frac{\tanh(\xi_{i})}{\xi_{i}} (3\xi_{i}^{5} + 6\xi_{i}^{3}) \right)$$
(S9)

$$J = 2\xi_i^2 + 3 - 3\frac{\tanh(\xi_i)}{\xi_i}$$
(S10)

In Eqs. (S8-S10) and their consequent equations, the subscript *i* has not been placed for parameters for the sake simplicity.

The Brinkman permeability model^{2, 3, 10, 11} is given as:

$$\kappa_{i} = \frac{(a_{0})^{2}}{18} \left(3 + \frac{3}{(1 - \varphi_{i})} - \left(\frac{8}{(1 - \varphi_{i})} - 3 \right)^{\frac{1}{3}} \right)$$
(S11)

where porosity, φ_i , is determined from:^{5, 10, 12}

$$\varphi_i = 1 - \left(\frac{a_i}{a_0}\right)^{D_f - 3} \tag{S12}$$

where a_0 is the primary particle radius [L] and a_i is an aggregate radius in size class *i* [L].

The settling velocity of each aggregate in size class k, U_k , can be calculated from an empirical power law equation that is based on fractal dimension:¹³⁻¹⁵

$$\frac{U_k}{U_0} = \left(\frac{a_k}{a_0}\right)^{D_{sed}}$$
(S13)

where U_0 is the sedimentation velocity of primary particles [LT⁻¹] and D_{sed} is the sedimentation exponent which can be expressed in terms of fractal dimension of aggregates via various empirical relationships.¹⁴ The most frequently-used expression is:^{15, 16}

$$D_{sed} = D_f - 1 \tag{S14}$$

 U_0 is the settling velocity for primary particles [L T⁻¹], and can be determined from the Stokes' equation:¹⁷

$$U_0 = \frac{2g}{9\mu} (\rho_0 - \rho_w) a_0^2$$
(S15)

where g is the gravitational acceleration, ρ_0 is density of primary particles, [ML⁻³], and ρ_w is density of water [ML⁻³]. Combination of these equations yields:¹²

$$U_{k} = \frac{g}{18\mu} (\rho_{0} - \rho_{w}) (2a_{0})^{3 - D_{f}} (2a_{k})^{D_{f} - 1}$$
(S16)

Details of the MATLAB code for simulating the aggregation and sedimentation of nanoparticles.

The primary particle size is used as the first bin size in the aggregation modeling process. Additionally, this primary particle radius, a_0 , is used in the calculations of sedimentation velocity and collision rates. We assume this size as the minimum of the following two sizes:

- a. The minimum initial hydrodynamic diameter observed among different experimental cases. This size is 90 nm for SGO used in the present study.
- b. The minimum size of the PSD bins which has a non-zero concentration in the initialmeasured PSD, i.e., PSD at time zero. This size varies among different cases with different initial PSDs.

A mass- or solid volume-weighted geometrical mean approach is used to calculate the average diameter of PSD produced by the model at different times.¹⁸ This geometric mean diameter, D_{geom} , is as follows:

$$D_{geom} = exp\left(\frac{\sum_{i=1}^{k_{max}} C_i d_i^{\ 3} \ln d_i}{\sum_{i=1}^{k_{max}} C_i d_i^{\ 3}}\right)$$
(S17)

where *C* is the mass concentration in each bin and *d* is aggregate size class diameter. To convert this average size to the hydrodynamic size, we determined the ratio of the initial experimental hydrodynamic size to the model-calculated geometric mean size (R_H/R_g). Then this ratio is utilized to convert all the geometric mean sizes over the duration of simulation to the hydrodynamic size that can be used as model output for comparing with observed hydrodynamic size data.¹⁹

The solid volume of each bin, is obtained from the size of each bin following:¹²

$$\nu_k = \frac{\pi}{6} (d_0)^{3-D_f} (d_k)^{D_f}$$
(S18)

where d_0 and d_k are the diameters of primary particle and the aggregates size class k. The mass of aggregates in each size class, m_k , is determined from:¹²

$$m_k = \rho_0 v_k \tag{S19}$$

An explicit forward Euler scheme was used to solve the governing equation of aggregation (Eq. 9):²⁰

$$n_{k,t} = n_{k,t-\Delta t} + \Delta t \frac{dn_{k,t-\Delta t}}{dt}$$
(S20)

where Δt is the time discretization interval. The model by default considers the bin size distribution that is also used by the DLS instruments, Malvern ZetaSizer, Nano ZS model, UK. Further information regarding the adjustment of Δt is available in the previous report.¹⁹ The models were already¹⁹ validated against analytical solution of the aggregation model in two types of initial conditions.

Parameter estimation algorithm. To calibrate the parameters of the model, which comprise of attachment efficiency and fractal dimension, a heuristic optimization algorithm developed in the previous study¹⁹ was used here too. This algorithm has two advantages: (1) it can deal with potential stability problems of the numerical code and (2) it utilizes the parallel computational capability more efficiently in the calibration process. In brief, this algorithm consists of two major loops. In the first loop the Nash-Sutcliff R^{2} ,²¹ as an objective function, is elevated iteratively until the difference between R^2 in two successive iterations is below 0.1. In the second loop, the similar procedure is pursued with more refined parameter increments until the difference between R^2 in two successive iterations reaches below 0.01. In each loop, the parameter values are multiplied by a series of 5 factors, and the model is run for each value. The multiplication which results in the best R^2 is exerted in the next iteration. It is important to note that in each iteration only one multiplication which results in the best R^2 among all multiplications in the two parameters is selected for the next iteration. In other words, only one parameter can be changed in each iteration. The stability issue of the explicit numerical code was mostly arisen when a combination range of the two parameters led to very high rate of aggregation and low rate of sedimentation which cannot occur in realistic experimental conditions but could be encountered in the automatic parameter calibration process. For these cases the optimization algorithm, acting as a 'master' model, was designed to decrease the time step of the numerical code, acting as a 'slave' model, if this goes unstable. Additionally, the scheme considers if after three increments in the time step size the model was still unstable, the optimization algorithm skipped that multiplication of the parameter value.

Unlike the other automatic calibration schemes in which noise or instability issues can hinder the calculation of parameter gradients,^{22, 23} in the present approach, skipping the unstable runs could not prevent finding the final optimum parameter values. Similar to other optimization techniques,²⁴ feeding the model with appropriate initial values of parameters was important, especially, the model should be stable in the initial values of parameters fed to the optimization model. This stable initial condition causes the optimization model goes ahead without being hindered by unstable runs. This is because a factor of one is among the five parameter value multiplications, and thus from the beginning to the end of the parameter calibration process always there is at least one set of parameter values for which the model produces correct outputs. If the increments in the first

major loop met the requirement of the loop or fail to find any stable solution, then the optimization procedure proceeds to the second loop. In this loop, more refined multiplications enhance the fit and a greater chance of finding a stable solution is offered since the parameters adopt closer values to the stable ranges. The ability of the parallel runs of the model for incremented parameter values is believed to enhance the total run time significantly.

It should be noted that Nash-Sutcliff R^2 might not perform very well as an objective function. Especially, we noticed that when the distance of the data points with the horizontal axis is small, even though visually a good match is achieved between the two graphs of the observation and modeled data, Nash-Sutcliff R^2 is not showing a value close to one as expected to show. This can cause difficulty for the optimization code to find the best set of parameters in such cases. Yet we found that with reducing the criteria of R^2 difference in two successive iterations (e.g., from 0.1 to 0.001 in the first loop), the algorithm was still able to find the optimum parameter values in such cases. In future uses this objective function can be simply replaced with sum of squared errors (SSR) which should be minimized within the optimization process.

Figures and Tables:



Figure S1. The experimental setup used in this work (a) and an enlarged photograph of the cylinder (b). The diameter of the cylinder shown in the panel (a) is 8.2 cm which was manufactured for initial trials of the investigation while that shown in panel (b) is



Figure S2. Experimental photos of the cylinder ($a_{cyl}=2.5$ cm) rotating at 4.71 rph corresponding to *Re*=0.91 after Methylene Blue injection.



Figure S3. (a) The rotational component of velocity and (b) shear rate vs distance from the centre of the cylinder for the cylinder at different times.



Figure S4. Velocity vectors for various D_f and particle radii.



Figure S5. Experimental photos of SGO aggregation over longer times for the case of rotating cylinder filled with SGO NP in 0.75 mM CaCl₂ solution and pH 6.



Figure S6. Variation of nondimensionalized collision frequency calculated for collision between particles/aggregates with radii 50 (a), 500 (b), or 2000 (c) nm with all other particle size classes for different fractal dimensions. Other input parameters of the aggregation model assumed as: attachment efficiency α =1, particle density 1800 Kg/m³, and shear rate G=0. τ is the characteristic time of aggregation ²⁵ and n_0 is the initial population of particles.

Ionic strength	Condition	α	D_f	R^2_{NS}
0.5	control	7.0E-06	1.36	0.709
	static	1.0E-05	1.38	0.433
	dynamic	4.9E-05	1.53	0.814
0.75	control	6.5E-04	1.34	0.870
	static	1.1E-03	1.82	0.776
	static	1.2E-04	1.40	0.960
	dynamic	1.4E-03	2.06	0.578
	dynamic	6.8E-03	2.63	0.921

Table S1. Parameter values estimated in the fitting process together with Nash-Sutcliff goodness-of-fit criterion, R^2_{NS} .

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