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Aggregation of Elongated Colloids in Water

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Abstract

Colloidal aggregation is a canonical example of disordered growth far from equilibrium and has been extensively studied for the case of spherical monomers. Many particles encountered in industry and the environment are highly elongated; however, the control of particle shape on aggregation kinetics and structure is not well-known. Here, we explore this control in laboratory experiments that document aqueous diffusion and aggregation of two different elongated colloids: natural asbestos fibers and synthetic glass rods, with similar aspect ratios of about 5:1. We also perform control runs with glass spheres of similar size ($\sim 1 \mu\text{m}$). The aggregates assembled from the elongated particles are noncompact, with morphologies and growth rates that differ markedly from the classical aggregation dynamics observed for spherical monomers. The results for asbestos and glass rods are remarkably similar, demonstrating the primacy of shape over material properties—suggesting that our findings may be extended to other elongated colloids such as carbon nanotubes/fibers. This study may lead to enhanced prediction of the transport and fate of colloidal contaminants in the environment, which are strongly influenced by the growth and structure of aggregates.

Graphical abstract

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Introduction

The self-assembling of colloids to form large aggregates is a phenomenon central to many natural and synthetic processes.^{1–4} Over the past few decades, there has been a growing interest in developing a unified description of such processes.^{5–8} For a variety of colloidal systems, two limiting regimes of aggregation kinetics have been modeled: (i) diffusion-limited aggregation (DLA), in which every collision between the particles results in the formation of a bond⁹ and (ii) reaction-limited aggregation (RLA), in which only a small fraction of particle collisions leads to the formation of a bond⁷. Each regime is characterized by distinctly different structures and growth dynamics. Recently, in situ microscopy, coupled with automated image analysis, has allowed direct observation of particle-by-particle growth of aggregates.^{10–12} These observations have provided quantitative confirmation of DLA and RLA models for many colloidal systems but have also revealed nonclassical aggregate growth mechanisms.

The vast majority of studies have examined the aggregation of near-spherical particles, whose diffusion and attachment dynamics are isotropic. Recently, however, researchers have begun to recognize the importance of shape in colloidal self-assembly.^{1,2} The elongated particles have many industrial applications and are abundant in the natural aquatic environment and cell (Figure 1A,B).^{13,14} For example, asbestos particles—contaminants whose aspect ratios (length/diameter) range from 2 to 100—typically reside in soil that is at least partially saturated, and the aggregates formed in the aqueous phase may influence the mobility of particles in the environment.¹⁵ The elongated particles exhibit anisotropic diffusion,¹⁶ and their shape may also affect the spatial distribution of charges on the particle surface.¹⁷ These factors may significantly influence the strength and direction of monomer attachment, whereas additional geometric effects¹⁸ likely play a role in the structure of aggregates. Although the aggregates formed from elongated particles are well-known,¹⁹ quantitative studies on their growth kinetics and structure are rare. Simulations and experiments by Mohraz et al. found that aggregate fractal dimension increased with monomer aspect ratio;¹⁸ however, Rothenbuhler et al.²⁰ reported simulations in which the clusters formed from long rods and thin disks were less dense than those formed by more compact particles.

To isolate the effects of monomer shape on the formation and geometry of aggregates, experimental observations of the particle-by-particle assembly are needed. Here, we examine solution-phase aggregation kinetics of the elongated colloids in water, over micron-to-centimeter length scales and from a tenth of a second to hours. To determine the sensitivity of aggregation to material properties and shape, we study two different elongated particles: natural chrysotile asbestos fibers, with heterogeneous size and composition; and uniform glass (silica) rods. We also perform control experiments with glass spheres. The growth and structure of aggregates formed from asbestos and glass rods are remarkably similar and significantly different from those of aggregates formed from glass spheres. The measurements and theory indicate that colloid attachment is stronger for rods when compared with spheres, which may be a consequence of the enhanced charge heterogeneity owing to an elongated shape. The aggregates formed from the elongated particles are sparse and noncompact, and their size distribution differs significantly from Smoluchowski growth kinetics. Although the precise mechanisms responsible for these differences are not yet resolved, our results show that particle shape exerts a primary control that is independent of colloid material properties and provides a new target for future modeling efforts.

Results

Experimental Setup

Experiments were conducted using a liquid cell mounted on a 100 $\times$ -magnification inverted optical microscope (Figure 1C). To test for the control of interparticle attraction on aggregation dynamics, we varied the pH of a subset of experiments from 3.6 to 8.0. A dilute suspension with a fixed concentration of 150 ppm of the target colloid was first prepared by mixing particles in a solution of water, dispersing particles using a sonicator, and then adjusting pH by titration with HCl. The zeta (ζ) potential for each solution was measured to quantify electrostatic repulsion for later analysis (see Materials and Methods). The solution was then delivered to the cell, which was sealed and mounted onto the stage of the microscope. This procedure typically took 2 min, so that the initiation of experimental observations at $t = 0$ corresponds to 2 ± 0.5 min after titration. Images with resolution ~ 0.90 μm were taken every 10 s until the aggregate growth saturated, with the experimental durations of up to 20 h. At the end of each experiment, a 4×4 grid of images was taken and stitched together to collect larger statistics of the size and shape of mature aggregates (see Materials and Methods) under steady-state conditions; particle-size distributions and morphology measurements presented below were obtained from these images. Our image analysis examined a two-dimensional (2D) slice near the bottom of the cell, so therefore, results do not capture the 3D structure of aggregates, and the observed dynamics may be influenced slightly by sedimentation. Particles and clusters (aggregates) were identified and separated in each image using a suite of shape properties. We tracked the motion of individual colloids and aggregates in the focal plane using a morphological image processing algorithm, as described in our previous work.²¹ A customized autocorrelation analysis determined the particle-size distribution for each image (see Materials and Methods). Chrysotile asbestos fibers had an average diameter and length of $d = 1.9 \pm 0.5$ μm and $L = 10 \pm 0.8$ μm , respectively, with lengths ranging up to 20 μm . The glass rods were more uniform in size with $d = 2$ μm and $L = 8$ μm , respectively, and the glass spheres had a

diameter $d = 2.9 \mu\text{m}$ (see Materials and Methods). Particle sizes were chosen, so that their masses would be comparable. Figure 1D–F shows representative bright-field images of the aggregates formed by colloidal particles with different monomer geometries.

Aggregate Growth Curve

The growth of the average cluster size λ (see Materials and Methods) through time was examined for each experiment, with some representative runs plotted in Figure 2A. In all experiments, we observed a significant dormant period preceding the onset of aggregation (phase I, also referred to elsewhere as the “lag phase”²²). At this initial stage, we verified that individual particles were undergoing Brownian motion (see ref 21). During the next growth period (phase II), these diffusing particles collided with and separated from neighboring particles multiple times, driving net aggregation. The individual particles always grew with time and were never observed to dissolve. In the late stage (phase III), the characteristic length λ increased by $\sim 50\%$, consistent with a prior work¹² and reached a saturated value. Our observations show that the aggregates stopped growing because of a finite particle supply.

For classical DLA, the characteristic aggregate size grows with time as $\langle r \rangle = Kt^{\langle \beta \rangle}$, where the growth exponent has been reported as $\langle \beta \rangle = 0.31 \pm 0.1$.^{7,23,24} Given the limited range of growth seen in our experiments because of saturation, we cannot confidently fit the growth curves to quantitatively test this relation. Nonetheless, growth curves for spherical monomers are consistent with this result (Figure S3). For the range of pH values tested, the growth curves for asbestos fibers and glass rods are nearly identical and are distinct from those of spheres (Figure 2A). While the data range is limited, growth curves for the two elongated particles are inconsistent with DLA predictions, suggesting that diffusion may not be the only mechanism driving growth. The characteristic length evolves to the same asymptotic value $\lambda \approx 4.3 \mu\text{m}$ for asbestos fibers and glass rods. Changing pH has the effect of shifting the growth curves, such that lower pH values result in faster aggregation kinetics (Figure 2B). Faster growth in this case can be explained on the basis of surface-charge screening, resulting in higher collision rates (see below). However, by normalizing aggregation time t using a characteristic aggregation time (t_{50}), the growth curves collapse (Figure 2C), indicating similar growth dynamics for the two elongated particles tested. The similarity of the growth curves for asbestos fibers and glass rods, and their difference from observations of glass spheres, indicates that shape exerts a significant influence on aggregation dynamics. The characteristic aggregation time is a useful parameter to estimate whether a given suspension is stable within an experimental time window or not. When t_{50} is much larger than the experimental window, the suspension is stable, whereas when t_{50} is much smaller, the suspension will be unstable. We use this experimental time scale to compare with the theoretical predictions below.

Aggregate Morphology

A common metric for aggregate morphology and structure is the fractal dimension α ,²⁵ which may be computed as the power-law exponent in the relationship between the particle area (A) and the radius of gyration (R_g), $A \propto R_g^\alpha$. For two-dimensional solid objects $\alpha = 2$, a value less than 2 indicates a fractal structure whose density decreases as α decreases. We

expect that $\alpha \approx 2$ for length scales below the diameter of a monomer, whereas $\alpha < 2$ for scales between that of a monomer and the characteristic size of an aggregate. We determine the scaling $A \propto R_g^\alpha$ for all experiments with asbestos fibers, glass rods, and glass spheres from image mosaics at the end of each experiment (see Materials and Methods); representative plots are shown in Figure 3. All three materials show the expected scaling behavior: $\alpha \approx 2$ below a cutoff length that is close to the monomer diameter, while data are well-fit with a power law of $\alpha < 2$ for the range of scales corresponding to the clusters, indicating that the aggregates may all be described as scale-invariant objects. For representative experiments at pH = 5.0, the fractal exponents of the two elongated particle species are nearly identical (1.71 ± 0.01 and 1.69 ± 0.01 for asbestos and glass, respectively) and significantly lower than that of the spheres (1.83 ± 0.01) (Figure 3D–F). Fractal dimension decreases slightly with an increasing pH for all species, indicating that stronger interparticle repulsion creates sparser aggregates; however, the magnitude of the pH effect is much smaller than that of the shape (Table S1). A note of caution is warranted when interpreting these 2D fractal exponents, however, because they were determined from planar images of 3D objects. Nonetheless, relative comparisons can be made.

The fractal dimension of aggregates formed by the elongated monomers is smaller than previous values reported for the spheres and is consistent with the observed extended stringy morphologies and loose dendrite structures (Figure 3A,B). These effects may arise from the repulsive interactions between rodlike particles, which have been proposed to favor linear rather than branched configurations of clusters.²⁰ The similar scaling for the aggregates formed from asbestos fibers and glass rods indicates that elongation influences the aggregate structure in a manner that is independent of materials and is only weakly sensitive to pH. The higher fractal dimension formed by the spherical particles suggests more compact and globular shapes (Figure 3C), and the value for spheres is in good agreement with previous studies.^{7,8,25,26}

Aggregate Size Distributions

We then consider the cluster size distributions for the same pH = 5.0 experiments presented above. The cumulative size distributions for each experiment are normalized by their respective mean values, that is, $n/\langle n \rangle = 1$, to facilitate direct comparison (Figure 4). All experiments show that the data are skewed to the right of the mean, indicating that the dominant mode of the cluster growth at later times is cluster collision and coalescence, which was also confirmed by direct observation (Movies S1–S3). Again, we see that the results for asbestos fibers and glass rods are very similar to each other, and depart from the results for spheres, and also that the distribution is weakly sensitive to pH (Figure S2). The deviations are most significant for the coarse tail of the distribution, where data suggest that the elongated monomers have a heavier-tailed distribution than the spheres. We compare the particle-size distributions to what is expected for Smoluchowski kinetics, a classical model that describes the time evolution of an ensemble of particles as they aggregate²⁷. A characteristic analytical solution for the particle-size distribution in the long-time limit can be written as²⁸

$$F(\varphi) = \frac{2W}{\Gamma(\sigma+1)} (W\varphi)^{2\sigma+1} e^{-(W\varphi)^2} \quad (1)$$

$$W = (\sigma+1) \frac{\Gamma(\sigma+3/2)}{\Gamma(\sigma+2)} z \quad (2)$$

where $F(\varphi)$ is the analytical particle-size distribution scaled to the average particle size, $\varphi = r/\langle r \rangle$, Γ is the standard Gamma function, and σ is the scaling exponent for particle/cluster diffusion. Previous studies indicate that the scaling exponent for Brownian particles and clusters is $\sigma = 1/2$.²⁸ We applied this value in our calculations. It is clear that the Smoluchowski model deviates from all observations; in particular, it overestimates the number of clusters smaller than the mean (i.e., $r < \langle r \rangle$ or $\varphi < 1$) and underestimates the number of clusters that are larger than the mean $\langle r \rangle$. Despite these discrepancies, the Smoluchowski model provides a decent approximation of the size distribution for spherical particles. Elongated particles indicate that the Smoluchowski model is inadequate, whereas the similarity of asbestos fibers and glass rods again suggests that the reason for this difference is related to shape rather than material properties.

Time Scale of Aggregation

As discussed previously, pH has a significant effect on the aggregation kinetics. We attempt to explain this effect by considering the interaction potential between two charged particles as described by the classical Derjaguin–Landau–Verwey–Overbeek (DLVO) theory, which includes van der Waals and electrostatic double-layer interactions. A primary assumption in the DLVO framework is that the particles are spherical; however, both van der Waals and electrostatic double-layer forces are affected by changes in shape.^{34,35} At a separation distance smaller than the mean diameter, the attraction between the elongated particles is expected to be larger than for the spherical particles of equal volume because a greater number of atoms are in close proximity. Electrostatic double-layer forces of cylindrical particles are also in principle as a function of particle orientation. These results imply that an elongated shape may enhance aggregation under some favored orientations.³⁶

We measured the surface ζ potential for glass rods and spheres over a range of pH values, $3.6 < \text{pH} < 8.0$ (Figure 5B). ζ potential values are increasingly negative with an increasing pH and are compatible with the isoelectric point (IEP) values ($\sim 2\text{--}3$) reported in the literature for pure silica materials.³⁷ The values indicate that aggregation should be possible over the whole range of pH values but would be expected to progressively slow with an increasing pH—consistent with our observations and that the ζ potential of silica rods is slightly more negative than that of silica spheres under the same pH conditions is due to two possible reasons: (1) the specific surface area of silica rods is slightly larger than that of silica spheres in the study, and (2) the cylindrical shape may cause heterogeneity of charge distribution and hence surface potential measurements. We also examined the dependence of ζ potential on pH for chrysotile. It is interesting that the IEP value of chrysotile fibers

treated by dilute acetic acid in this study²¹ is about 4–5, which is lower than the IEP values for the pristine chrysotile fibers reported elsewhere [e.g., IEP $\sim$ 6–7 (chrysotile basal plane) and IEP $\approx$ 10–11 (chrysotile edge plane)].¹⁵ This result could be attributed to the deliberate acid-leaching of chrysotile fibers, which ultimately drives the ζ potential to turn from positive to negative.³⁸ This result also, to some extent, explains why the growth curves of chrysotile fibers and silica rods are similar. The measured ζ potentials were used to calculate the interaction energy ϕ between sphere–sphere and rod–rod configurations (see Materials and Methods); Figure 5A illustrates an example calculation of the energy profile as a function of distance at pH 5.0. Previous studies indicate that for elongated particles, h is dependent on the contact configuration and that the crossed configuration presents the lowest repulsive energy³⁹ (Figure 5C); we choose this configuration to compute the theoretical aggregation time scale of silica rods (see Materials and Methods). The comparison of theoretical and experimental time scales of aggregation suggests that the classical DLVO theory provides a good estimate of aggregation kinetics under favorable conditions (low energy barrier and pH) but increasingly overestimates the interaction energy for both silica rods and silica spheres as the energy barrier (and pH) increases. These results indicate that the experimental aggregation kinetics are faster than that expected for unfavorable conditions. At the highest pH values, this difference is around a factor of 2 for spheres and up to 10 for rods. In other words, even assuming that all rods interact under the most favorable configuration results in a large overprediction in the growth rate. Recent research has indicated that surface-charge heterogeneity can allow aggregation under conditions predicted to be unfavorable by DLVO theory, which assumes that the charges are distributed uniformly across the particle surface.⁴⁰ If this is the cause of the discrepancy between the theoretical and the experimental aggregation time scales—which seems reasonable—then one may expect that an elongated shape may lead to even more charge heterogeneity; however, this possibility cannot be confirmed at present.

Discussion and Conclusions

The morphology, growth, and size distribution of the aggregates formed from spherical monomers are in reasonable agreement with the classical growth models—in particular, DLA and Smoluchowski kinetics. Elongated particles, however, are not. The size distribution of clusters made up of elongated monomers is wider than that expected from Smoluchowski growth kinetics, and the resultant fractal aggregate structure is less dense than structures composed of spherical monomers. The growth curves for the aggregation of elongated particles differ substantially from that of spheres. Both spheres and elongated particles depart from the theoretical (DLVO) predictions for the time scale of aggregation, an effect that has recently been proposed to result from surface-charge heterogeneity.⁴⁰ The difference is substantially larger for the elongated particles; however, the magnitude of the effect depends on the choice of particle-interaction configuration.

The low-dimension aggregate structures formed by elongated particles are not fully explained by either the DLA or RLA mechanisms, indicating that more complex particle-interaction mechanisms must be present here. In particular, the local-particle-scale structure and dominant collision types depend strongly on monomer geometry and its anisotropic diffusion,^{16,21} which could be further explored by future simulations. Another possible

modeling avenue is that a time-dependent or anisotropic collision kernel could be included in the Smoluchowski kinetic model to account for the influence of cluster–cluster interactions that appear to result from the particle shape effects.

Perhaps, the most remarkable finding is the quantitative similarity of aggregation structure and kinetics between the chrysotile asbestos fibers and the glass rods. The natural asbestos fibers are certainly heterogeneous in their length and presumably also in their shape and composition. The glass rods have uniform size, shape, and composition; the latter being quite different from chrysotile. Despite these differences, they show virtually identical behavior in terms of growth curves, fractal dimension, and size distribution. This comparison demonstrates that shape and not material is the factor responsible for deviations from classical aggregation dynamics, and that characterizing these shape effects is crucial for improving the prediction of elongated-colloid aggregation in natural and engineered systems. Results are robust for a wide range of pH. This opens the door to quantitative prediction of aggregation for a wide range of nonspherical particles, including manufactured colloids such as carbon nanotubes;⁴¹ biological particles such as blood cells⁴² and proteins;⁴³ and the flocculating muds that form marshes, estuaries, and river deltas.⁴⁴ The sparse aggregate structure may have important implications for transport and stability in the environment. For example, aggregates with low fractal dimension are less susceptible to gravitational settling and are more optically transparent.^{45,46} Whether they are more or less stable under fluid shear, such as that experienced in flow through soil or rivers, is an open question.

Materials and Methods

Materials and Experimental Protocol

A raw chrysotile ore block (purity > 90%) from El Dorado Mine, Salt River, Arizona was used as the source material for generating fibers. The procedures for the preparation of a well-dispersed chrysotile fiber suspension were reported previously.²¹ Colloidal silica rods with approximately monodisperse dimensions were synthesized following the protocol reported in ref 47. Silica spheres were purchased from Polyscience, Inc. (Warrington, PA). Aggregation in stable aqueous suspensions was induced with pH. The reagents used to vary pH were HCl 0.1 mol/L and KOH 0.1 mol/L. The pH of the solutions was measured with an pH meter (ION 510 series, Oakton Instruments Inc., USA). The electrophoretic mobility measurements were recorded on a Delsa Nano C (Beckman Coulter Inc., USA), and the ζ potential was determined from the measured electrophoretic mobility, using the Smoluchowski approximation.⁴⁸ Depending on the magnitude of the ζ potential, the spherical Smoluchowski approximation may overestimate the actual ζ potential of elongated colloids by up to 20%.⁴⁹ The van der Waals force was approximated with the nonretarded van der Waals interaction for identical silica surfaces across water with a Hamaker constant of 1×10^{-20} J.²⁹ This value is generally acceptable and within the reported range of Hamaker constant for silica–water–silica system (0.24×10^{-20} to 1.7×10^{-20} J). The ζ potential of silica fibers, silica rods, and chrysotile fibers as a function of pH at 0.0001 M NaCl concentration (measured at 25 °C) is shown in Figure 5B. Images were acquired by a powerful inverted microscope system, Eclipse Ti-E, (Nikon Instruments Inc., USA), a 100×

oil-immersion objective (NA = 1.4, depth of focus = 0.5 μm), and a Andor iXon3 EMCCD camera controlled by NIS Elements software (Nikon Instruments Inc., USA).

Image Analysis

All analysis was performed in MATLAB, and codes used in this paper are available. We outline the steps here. First, we subtracted background noise from each image and then used Otsu's thresholding method to obtain binary images for the subsequent analysis of particle size evolution through time (Figure S1B). The autocorrelation length was determined from a customized algorithm based on the fast Fourier transform, whereas the error was estimated using a bootstrap resampling method. Processing of large image mosaics at the end of each experiment was different: a Niblack threshold criterion was used to make mosaics binary. Image segmentation was used to identify objects, and three shape parameters were calculated to separate individual particles from clusters (aggregates): area, solidity, and eccentricity (Figure S1E). The radius of gyration for each object was determined from the eigenvalues of the gyration tensor.

Determination of Characteristic Autocorrelation Length

After importing the source images, local standard deviation was implemented as a linear filtering. An image of an empty field was taken to assess the noise levels of the detector system, and the mean value of this noise was set to be the 0 value for the actual images. This step ensured that the background of real images is close to zero, while maintaining the fidelity of information-containing regions. Global image threshold using the Otsu's method was applied to generate binary images. We developed a customized autocorrelation function via fast Fourier transforms using the Wiener–Khinchin theorem

$$F^{-1}[G_{ii}(a, b)] = S(i) = |F[i(x, y)]|^2 \quad (3)$$

where $G_{ii}(a, b)$ is the autocorrelation function, $i(x, y)$ is the image intensity at position (x, y) , and a and b represent the distance (or lag) from the corresponding x and y position. $F(x, y)$ is the Fourier transform of $i(x, y)$. $S(i)$ is the power spectrum of the image. A bootstrap resampling method was used to evaluate the error and compute 95% percentiles of the resulting distribution estimator. Fitting autocorrelation data with a simple exponential decay model results in a decay length λ , which is proportional to a measurement of the radius of each cluster r estimated by A .

Processing of Large-Stitching Images

The steps involved in the preprocessing of the bright-field images are summarized in Figure S1. In the first step, the software imports the raw bright-field images and the image data are extracted and stored (Figure S1A). A global threshold using the Ostwald criterion was applied to convert the raw images to binary images (Figure S1B). The software identified all objects (including single particles and clusters) by image segmentation (MATLAB *bwlabel* function) (Figure S1C), and the objects are characterized using the MATLAB *regionprops* function and best fit with ellipses (Figure S1D).

Identification of Particles and Clusters

The procedure used to identify particles and clusters is illustrated in Figure S1E,F. Single particles are identified on the basis of three properties of the objects: area, solidity, and eccentricity. The area of an object is calculated as the number of foreground pixels occupying it. Solidity is calculated as the ratio of its area to the area of the smallest convex polygon completely enclosing the object. The solidity is calculated as the ratio of the filled area to the area of bounding box. The solidity_ellipse is calculated as the ratio of the filled area to the area of best fit ellipse. Finally, its eccentricity is calculated as the ratio of the distance between the foci of an ellipse that has the same normalized second central moments as the object and the major axis length of the ellipse (Figure S1E). The acceptable criteria used in our study to identify single particles and clusters are illustrated in Figure S1F,G, respectively. Figure S1H shows the combination of identified single particles and clusters.

Calculation of Aggregate Properties

We calculate the cluster size directly from area measurement A by counting the number of pixels in each identified cluster or single particle and by converting the measured pixels to real dimensions. To get statistically robust measurement of cluster properties, large image acquisition and stitching by Nikon NIS Elements built-in methods were applied to get stitched images, which are 4×4 larger than the image with a normal field of view. We also calculated the eigenvalues (principal moments) R_x^2 R_y^2 of the gyration tensor for each cluster. The eigenvalues are then used to compute the radius of gyration of the clusters, which characterizes their spatial extent and other useful properties, such as anisotropy. The radius of gyration can be determined by

$$R_g = \sqrt{(R_x^2 + R_y^2)} \quad (4)$$

The anisotropy FA can be determined by

$$FA = |R_x - R_y| \quad (5)$$

We calculated the self-similarity dimensions of a self-similar cluster by studying a family of similar but differently sized clusters to extract the scaling exponent. Specifically, we computed α by the following relationship

$$A \approx R_g^\alpha \quad (6)$$

where A is the estimated area of a cluster. Objects below the cutoff size determined for individual particles (dashed vertical lines in Figure 3D–F) are excluded from the regression used to determine the cluster fractal dimension; this ensures that polydispersity in individual particle sizes does not contaminate the results.

DLVO Interaction Energy and Time Scale of the Aggregation of Spherical and Rodlike Particles

For the case of silica spheres, the expressions of classic DLVO interaction energy were used for calculations of electrostatic and van der Waals interaction energies.^{50,51} The interaction energy for silica rods was calculated using the DeJaguin approximation, which can be applied to arbitrary-curved colloid shapes and expressed as^{52,53}

$$\Phi(h) = \frac{2\pi}{\sqrt{\lambda_1 \lambda_2}} \int_h^\infty E(h) dh \quad (7)$$

where $\Phi(h)$ is the interaction energy between the curved surfaces 1 and 2, $E(h)$ is the interaction energy between two flat plates separated by distance h , and λ_1 and λ_2 are constants, characterizing the geometry of the curved surfaces 1 and 2, respectively. h is the distance of the closest approach between the curved surfaces. The geometrical factor $\lambda_1 \lambda_2$ for interactions between rodlike particles is complex and depends on the orientation of particles but is related to the particle aspect ratio for parallel and perpendicular orientations. In the case of electrostatic repulsion, the particles will preferably adsorb under the perpendicular orientation. Furthermore, our real-time observations of aggregate growth and final aggregate structure analysis indicate that the parallel configuration is not the dominant mode for particle-particle interactions in our study. Thus, we used cross-orientation configuration for rod-rod interactions. In this case $\lambda_1 \lambda_2 = 2r_{\text{rod}}$, where r_{rod} is the radius of rods. The net interaction including van der Waals attraction and electrostatic repulsion is given by⁵⁴

$$E(h) = \frac{2\varepsilon\psi_1\psi_2}{\kappa} \exp\left(-\frac{z}{\kappa}\right) - \frac{H}{12\pi z^2} \quad (8)$$

where ε is the dielectric constant, ψ is the surface potential on the charged surface (estimated from ζ potential measurements), κ is the Debye length, and H is the Hamaker constant. As one increases the surface potential ψ or the Debye length κ^{-1} , the local maximum in ϕ becomes increasingly positive. When $\phi_1/k_B T \gg 1$, particles that are initially separated from each other rarely acquire enough kinetic energy to surmount the high repulsive potential barrier (ϕ_1) and fall into the deep van der Waals primary minimum. Previous studies indicate that attachment in the secondary minimum (ϕ_2) is important for micron-sized colloids.^{55,56} Therefore, the probability that a particle-particle collision will be energetic enough to overcome the total barrier ($\phi_T = \phi_1 + \phi_2$) is proportional to $\exp[-\phi_T/k_B T]$ (Figure 5A). Because the time scale for a particle to diffuse a distance h is $\sim h^2/D_p$, where h is the shortest separation distance between individual particles and D_p is the diffusivity of the particle, the theoretical characteristic aggregation time can be written as⁵⁷

$$T_{\text{theo}} \approx \frac{h^2}{D_p} \exp\left(\frac{\Delta\phi_T}{K_B T}\right) \quad (9)$$

Note that for rods, diffusion is anisotropic; the appropriate diffusivity to use for our chosen interaction configuration is that associated with the shortest axis.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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References

1. Dugyala VR, Daware SV, Basavaraj MG. Shape anisotropic colloids: Synthesis, packing behavior, evaporation driven assembly, and their application in emulsion stabilization. *Soft Matter*. 2013; 9:6711–6725.
2. Sacanna S, Pine DJ, Yi GR. Engineering shape: The novel geometries of colloidal self-assembly. *Soft Matter*. 2013; 9:8096–8106.
3. Xiong C, Friedlander SK. Morphological properties of atmospheric aerosol aggregates. *Proc Natl Acad Sci USA*. 2001; 98:11851–11856. [PubMed: 11592995]
4. Glotzer SC, Solomon MJ. Anisotropy of building blocks and their assembly into complex structures. *Nat Mater*. 2007; 6:557–562. [PubMed: 17667968]
5. Lin MY, et al. Universality of fractal aggregates as probed by light scattering. *Proc R Soc London, Ser A*. 1989; 423:71–87.
6. Sandkuhler P, Lattuada M, Wu H, Sefcik J, Morbidelli M. Further insights into the universality of colloidal aggregation. *Adv Colloid Interface Sci*. 2005; 113:65–83. [PubMed: 15935139]
7. Martin JE. Slow aggregation of colloidal silica. *Phys Rev A: At, Mol, Opt Phys*. 1987; 36:3415.
8. Robinson DJ, Earnshaw JC. Experimental study of colloidal aggregation in two dimensions. I. Structural aspects. *Phys Rev A: At, Mol, Opt Phys*. 1992; 46:2045.
9. Martin JE, Wilcoxon JP, Schaefer D, Odinek J. Fast aggregation of colloidal silica. *Phys Rev A: At, Mol, Opt Phys*. 1990; 41:4379.
10. Grogan JM, Rotkina L, Bau HH. In situ liquid-cell electron microscopy of colloid aggregation and growth dynamics. *Phys Rev E: Stat, Nonlinear, Soft Matter Phys*. 2011; 83:061405.
11. Mohraz A, Solomon MJ. Direct visualization of colloidal rod assembly by confocal microscopy. *Langmuir*. 2005; 21:5298–5306. [PubMed: 15924453]
12. Woehl TJ, et al. Direct observation of aggregative nanoparticle growth: Kinetic modeling of the size distribution and growth rate. *Nano Lett*. 2014; 14:373–378. [PubMed: 24325680]
13. Schierle GSK, et al. In situ measurements of the formation and morphology of intracellular β -amyloid fibrils by super-resolution fluorescence imaging. *J Am Chem Soc*. 2011; 133:12902–12905. [PubMed: 21793568]
14. Guo L, Santschi PH, Balnois E, Wilkinson KJ, Zhang J, Buffle J. Fibrillar polysaccharides in marine macromolecular organic matter as imaged by atomic force microscopy and transmission electron microscopy. *Limnol Oceanogr*. 1998; 43:896.
15. Yang D, et al. Probing anisotropic surface properties and interaction forces of chrysotile rods by atomic force microscopy and rheology. *Langmuir*. 2014; 30:10809–10817. [PubMed: 25115179]

16. Han Y, et al. Brownian motion of an ellipsoid. *Science*. 2006; 314:626–630. [PubMed: 17068256]
17. Mantegazza F, Caggioni M, Jiménez ML, Bellini T. Anomalous field-induced particle orientation in dilute mixtures of charged rod-like and spherical colloids. *Nat Phys*. 2005; 1:103–106.
18. Mohraz A, Moler DB, Ziff RM, Solomon MJ. Effect of monomer geometry on the fractal structure of colloidal rod aggregates. *Phys Rev Lett*. 2004; 92:155503.
19. Solomon MJ, Spicer PT. Microstructural regimes of colloidal rod suspensions, gels, and glasses. *Soft Matter*. 2010; 6:1391–1400.
20. Rothenbuhler JR, Huang JR, DiDonna BA, Levine AJ, Mason TG. Mesoscale structure of diffusion-limited aggregates of colloidal rods and disks. *Soft Matter*. 2009; 5:3639–3645.
21. Wu L, Ortiz C, Xu Y, Willenbring J, Jerolmack D. In situ liquid cell observations of asbestos fiber diffusion in water. *Environ Sci Technol*. 2015; 49:13340–13349. [PubMed: 26461183]
22. Streets AM, Sourigues Y, Kopito RR, Melki R, Quake SR. Simultaneous measurement of amyloid fibril formation by dynamic light scattering and fluorescence reveals complex aggregation kinetics. *PLoS ONE*. 2013; 8(e54541)
23. Asnaghi D, Carpineti M, Giglio M, Sozzi M. Coagulation kinetics and aggregate morphology in the intermediate regimes between diffusion-limited and reaction-limited cluster aggregation. *Phys Rev A: At, Mol, Opt Phys*. 1992; 45:1018.
24. Shih WY, Liu J, Shih WH, Aksay IA. Aggregation of colloidal particles with a finite interparticle attraction energy. *J Stat Phys*. 1991; 62:961–984.
25. Broide ML, Cohen RJ. Experimental evidence of dynamic scaling in colloidal aggregation. *Phys Rev Lett*. 1990; 64:2026. [PubMed: 10041558]
26. Mohraz A, Moler DB, Ziff RM, Solomon MJ. Effect of monomer geometry on the fractal structure of colloidal rod aggregates. *Phys Rev Lett*. 2004; 92:155503. [PubMed: 15169295]
27. Smoluchowski MV. Drei Vorträge über Diffusion, Brownsche Bewegung und Koagulation von Kolloidteilchen. *Phys Z*. 1916; 17:557–585.
28. Sholl DS, Skodje RT. Late-stage coarsening of adlayers by dynamic cluster coalescence. *Phys A*. 1996; 231:631–647.
29. Rutland MW, Senden TJ. Adsorption of the poly-(oxyethylene) nonionic surfactant C12E5 to silica: A study using atomic force microscopy. *Langmuir*. 1993; 9:412–418.
30. Kobayashi M, Juillerat F, Galletto P, Bowen P, Borkovec M. Aggregation and charging of colloidal silica particles: Effect of particle size. *Langmuir*. 2005; 21:5761–5769. [PubMed: 15952820]
31. Hunter, RJ. *Foundations of Colloid Science*. Oxford University Press; 2001.
32. Israelachvili, JN. *Intermolecular and Surface Forces*. 3rd. Academic press; 2011.
33. Ackler HD, French RH, Chiang YM. Comparisons of hamaker constants for ceramic systems with intervening vacuum or water: From force laws and physical properties. *J Colloid Interface Sci*. 1996; 179:460–469.
34. Löwen H. Interaction between charged rodlike colloidal particles. *Phys Rev Lett*. 1994; 72:424. [PubMed: 10056427]
35. Wu L, Gao B, Tian Y, Muñoz-Carpena R, Zigler KJ. DLVO interactions of carbon nanotubes with isotropic planar surfaces. *Langmuir*. 2013; 29:3976–3988. [PubMed: 23442014]
36. Vold MJ. van der Waals' attraction between anisometric particles. *J Colloid Sci*. 1954; 9:451–459.
37. Júnior JAA, Baldo JB, et al. The behavior of zeta potential of silica suspensions. *New J Glass Ceram*. 2014; 4:29.
38. Chowdhury S, Kitchener JA. The zeta-potentials of natural and synthetic chrysotiles. *Int J Miner Process*. 1975; 2:277–285.
39. Choi JY, Dong HB, Haam SJ, Lee SY. Electrical repulsive energy between two cylindrical particles with finite length: Configuration dependence. *Bull Korean Chem Soc*. 2008; 29:1131–1136.
40. Pazmino E, Trauscht J, Dame B, Johnson WP. Power law size-distributed heterogeneity explains colloid retention on soda lime glass in the presence of energy barriers. *Langmuir*. 2014; 30:5412–5421. [PubMed: 24773424]
41. Barone PW, Strano MS. Reversible control of carbon nanotube aggregation for a glucose affinity sensor. *Angew Chem, Int Ed*. 2006; 45:8138–8141.

42. Riebesell U. Particle aggregation during a diatom bloom. II. Biological aspects. *Mar Ecol: Prog Ser.* 1991; 69:281–291.
43. Stefani M, Dobson CM. Protein aggregation and aggregate toxicity: New insights into protein folding, misfolding diseases and biological evolution. *J Mol Med.* 2003; 81:678–699. [PubMed: 12942175]
44. Van Leussen, W. *Physical Processes in Estuaries.* Springer; 1988. Aggregation of particles, settling velocity of mud flocs a review; p. 347–403.
45. Legg BA, Zhu M, Comolli LR, Gilbert B, Banfield JF. Determination of the three dimensional structure of ferrihydrite nanoparticle aggregates. *Langmuir.* 2014; 30:9931–9940. [PubMed: 25079430]
46. Gmachowski L. Aggregate structure and hydrodynamics of aggregated systems. *Colloids Surf, A.* 2005; 255:105–110.
47. Kuijk A, van Blaaderen A, Imhof A. Synthesis of monodisperse, rodlike silica colloids with tunable aspect ratio. *J Am Chem Soc.* 2011; 133:2346–2349. [PubMed: 21250633]
48. Hunter, RJ. *Zeta Potential in Colloid Science: Principles and Applications.* Vol. 2. Academic Press; 2013.
49. White B, Banerjee S, O'Brien S, Turro NJ, Herman IP. Zeta-potential measurements of surfactant-wrapped individual single-walled carbon nanotubes. *J Phys Chem C.* 2007; 111:13684–13690.
50. Hogg R, Healy TW, Fuerstenau DW. Mutual coagulation of colloidal dispersions. *Trans Faraday Soc.* 1966; 62:1638–1651.
51. Gregory J. Approximate expressions for retarded van der waals interaction. *J Colloid Interface Sci.* 1981; 83:138–145.
52. White LR. On the deryaguin approximation for the interaction of macrobodies. *J Colloid Interface Sci.* 1983; 95:286–288.
53. Bhattacharjee S, Chen JY, Elimelech M. DLVO interaction energy between spheroidal particles and a flat surface. *Colloids Surf, A.* 2000; 165:143–156.
54. Schiller P, Krüger S, Wahab M, Mögel HJ. Interactions between spheroidal colloidal particles. *Langmuir.* 2011; 27:10429–10437. [PubMed: 21780779]
55. Schowalter WR, Eidsath AB. Brownian flocculation of polymer colloids in the presence of a secondary minimum. *Proc Natl Acad Sci USA.* 2001; 98:3644–3651. [PubMed: 11274382]
56. Hahn MW, Abadzic D, O'Melia CR. Aquasols: On the role of secondary minima. *Environ Sci Technol.* 2004; 38:5915–5924. [PubMed: 15573589]
57. Russel, WB., Saville, DA., Schowalter, WR. *Colloidal Dispersions.* Cambridge University Press; 1989.

Figure 1.

Examples of fibrillar aggregates and experimental setup. (A) Optical microscopy image of β -amyloid fibril aggregates in a living cell;¹³ scale bar represents 1 μm . (B) Atomic force microscopy image of aquatic colloidal fibril aggregates from Middle Atlantic Bight (from 2500 m depth below the surface);¹⁴ scale bar represents 1 μm . The experimental setup (C) in this study and late-stage bright-field images showing the morphology of the aggregates formed by chrysotile fibers (D), silica rods (E) and silica spheres (F). The insets show individual monomers. (D–F) the same scale bar (10 μm).

Figure 2.

Growth of mean particle size by monomer attachment and aggregation. (A) Characteristic length of particles as a function of time for pH = 5.0. Chrysotile fibers, silica rods, and silica spheres are open diamonds, squares, and spheres, respectively. The insets show the particle/cluster morphologies at various phases for a representative chrysotile fiber experiment (phase I–phase III). (B) Characteristic length of clusters made up of silica rods as a function of time t under various pH conditions. Reflecting points τ_1 , τ_2 , and τ_3 represent characteristic half-aggregation time under pH = 4.3, 5.6, and 6.0, respectively. (C) Data from (B) where time has been normalized, t/τ_i ; data collapse indicates similarity of growth curves. Colors apply to all subsequent data.

Figure 3.

Morphology of the aggregates formed by asbestos fibers, silica rods, and silica spheres for pH = 5.0. (A–C) Planar projections of the detected aggregates at the end of each experiment (see Materials and Methods); arbitrary colors used to delineate clusters. (D–F) Log–log plots of average area A as a function of the radius of gyration R_g for data corresponding to (A–C). Data are best fit (least-squares fits are shown) by two scaling regimes, indicating solid particles ($\alpha \approx 2$) below the scale of a monomer diameter and fractal clusters ($\alpha < 2$) above that scale. Transition scale shown by vertical dashed line and diameter (d) of monomers indicated in figures.

Figure 4. Cluster size distributions, normalized by the mean, for aggregates formed by chrysotile fibers, silica rods, and silica spheres at the end of experiments with pH = 5.0. The solid black curve is the Smoluchowski particle-size distribution with $\sigma = 1/2$ using eqs 1 and 2.

Figure 5.

(A) Calculated DLVO interaction energies for silica rods and silica spheres as a function of separation distance h (nm) for pH = 5.0 conditions (see Materials and Methods). The total energy barrier that must be overcome for collision, $\phi_T = \phi_1 + \phi_2$, is indicated. For sphere and rod aggregation, we consider sphere-sphere and crossed rod-rod configurations, respectively, shown schematically in (C). ζ potentials of silica rods and spheres are -10.2 and -8.9 mV, respectively.^{29–33} The ionic strength for the suspensions was 0.0001 M. (B) ζ potential measurements of silica rods and silica spheres as a function of pH. Inset: comparison of ζ potential measurements of silica rods and chrysotile fibers. The error bars represent the standard deviation of three replicates for each run. (C) Comparison of theoretical (eq 9) and experimental characteristic aggregation time for silica rods and silica spheres under different pH conditions; the latter is estimated by the half-time of aggregation (t_{50}) determined from the growth curves. Experimental error was determined from autocorrelation length. Theoretical error was estimated by the error of ζ potential measurement. Color coding represents different pH values indicated by colorbar. Given well-dispersed dilute suspensions of silica spheres and rods, we assume the shortest distance h (eq 9) between individual spheres or rods is r_{sphere} and $L/2$, respectively. Note that rod diffusivity is anisotropic; for this configuration, the appropriate D_{rod} (eq 9) is determined along the short axis, as in our previous work.²¹