The attachment of colloidal particles to environmentally relevant surfaces and the effect of particle shape.

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Abstract

Despite the prevalence of nonspherical colloidal particles, the role of particle shape in the transport of colloids is largely understudied. This study investigates the attachment of colloidal particles onto environmentally relevant surfaces while varying particle shape and ionic strength. Using quartz crystal microbalance and atomic force microscopy measurements, the role of particle shape was elucidated and possible mechanisms discussed. The attachment of both spherical and stretched polystyrene colloidal particles onto a smooth alginate-coated silica surface showed qualitative agreement with DLVO theory. Attachment onto a Harpeth humic acid (HHA) surface, however, significantly deviated from DLVO theory due to its high surface heterogeneity and extended confirmation from the silica surface. This extended confirmation provided increased potential for spherical particle entanglement, while the enlarged major axis of the stretched particles hindered their ability to

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attach. As ionic strength increased, the HHA layer condensed and provided less potential for spherical particle entanglement and therefore the selectivity for spherical particle attachment vanished. The findings presented in this study suggest that colloidal particle shape may play a complex and important role in predicting the transport of colloidal particles, especially in the presence of natural organic matter-coated surfaces.

Keywords: QCM-D, transport, colloid shape, attachment, NOM

1. Introduction

Colloidal transport through the subsurface environment is a topic of great importance and intense study to the field of environmental engineering. Seemingly immobile toxins can attach to the surface of mobile colloids and be readily transported through the subsurface, greatly enhancing their risk to ecosystems and human health, or in some cases, the colloid itself is the toxin of concern (Ward et al., 1985). Many natural colloids are nonspherical in shape, including plate and rod shaped clay (Degueldre et al., 1996), various bacterial shapes (e.g. ellipsoid, ovoid, and rod shaped) (Hirsch and Rades-Rohkohl, 1990; Balkwill et al., 1989), and some engineered nanomaterials (e.g. carbon nanotubes) which exhibit an aquatic toxic potential (Nel et al., 2006). Despite the ubiquity of nonspherical colloids, only a limited number of studies have focused on the role of shape with regard to colloidal transport (Seymour et al., 2013; Baltus et al., 2008; Wang et al., 2008; Salerno et al., 2006; Weiss et al., 1995).

Weiss et al. (1995) demonstrated the systematic effect of bacterial cell shape on the transport of bacterial cells in packed columns and Salerno et al.

(2006) observed higher retention of polystyrene latex microspheres with increasing aspect ratio, illustrating the direct impact of particle shape on retention in porous media. Furthermore, two additional studies Baltus et al. (2008); Wang et al. (2008) examined the microfiltration of various types of bacterial cells, also demonstrating a sensitivity to cell shape, with Wang et al. (2008) suggesting that cell shape may be the determining factor in the filterability of bacteria. Aside from advection, dispersion, and diffusion, colloidal transport also depends on the kinetic rate at which particles attach to soil and grain surfaces with which they collide. To date, only one study has attempted to isolate the role of shape on particle deposition. Seymour et al. (2013) reported a much higher deposition rate of spherical carboxylate-modified polystyrene particles as compared to 2:1 and 4:1 stretched versions of the same particles. These experiments, however, were conducted under favorable conditions (i.e. a positively charged, PLL-coated silica surface), lacking an energy barrier to deposition and limiting the environmental relevance of the findings. No study to date has investigated the role of shape on colloidal particle attachment to environmentally relevant surfaces.

When dissolved in solution, NOM adsorbs to the surface of colloidal particles and typically limits their deposition through steric hindrance. When the depositional surfaces are pre-coated with NOM, however, the results tend to be much more complex. Pre-coating silica surfaces with various NOM have been shown to hinder, enhance, or have no effect on attachment, depending on the type of NOM (McNew and LeBoeuf, 2015; Chen and Elimelech, 2008), ionic strength of solution (Chang and Bouchard, 2013; Qu et al., 2012; Chen and Elimelech, 2008), and temperature (McNew and LeBoeuf, 2015).

Chen and Elimelech (2008) reported that an alginate layer enhanced nC₆₀ attachment in the presence of 10 mM NaCl, while hindering it in the presence of 30 mM NaCl. The variable nature was attributed to the alginate layer’s compaction at higher NaCl concentrations, resulting in a smoother, more rigid layer, with less room for nC₆₀ particle entanglement. In our recent work (McNew and LeBoeuf, 2015), we reported that increasing the temperature of a humic acid layer while holding all other variables constant, raised the attachment efficiency of nC₆₀ from low attachment ($\alpha = 0.3$) to complete attachment ($\alpha = 1$). We attributed this to the temperature-dependent hydration of the layer, opening up previously unavailable sorption sites.

Derjaguin-Landau-Verwey-Overbeek (DLVO) theory (Derjaguin, 1941; Verwey, 1947) describes the attractive and repulsive forces between a colloidal particle and a surface. Several studies have investigated the attachment of colloidal particles to bare mineral surfaces in simple electrolyte solutions (Chowdhury et al., 2014a; Chang and Bouchard, 2013; Shen et al., 2011; Yi and Chen, 2011; Jiang et al., 2010; Chen and Elimelech, 2008, 2006) and the results appear to be in good qualitative agreement with DLVO theory. The attachment deviates significantly from DLVO theory, however, in the presence of natural organic matter (NOM), whether dissolved in solution (Akaighe et al., 2013; Qu et al., 2012; Thio et al., 2011; Jiang et al., 2010; Chen and Elimelech, 2008) or coated onto the depositional surface (McNew and LeBoeuf, 2015; Chowdhury et al., 2014b; Chang and Bouchard, 2013; Thio et al., 2011; Qu et al., 2012; Jiang et al., 2010; Tong et al., 2010; Chen and Elimelech, 2008).

The purpose of this study is to isolate the role of shape on the attachment

of colloidal particles to environmentally relevant surfaces by combining quartz crystal microbalance with dissipation monitoring (QCM-D) and atomic force microscopy (AFM) experiments. For the first time, we present attachment efficiency curves for colloidal particles onto NOM coated silica surfaces, as a function of particle shape and ionic strength. By comparing the attachment results with DLS surface measurements and AFM topography images, we elucidate and discuss the mechanisms driving the complex attachment behavior observed. The results presented here suggest that colloidal particle shape will play an important role in predicting transport, especially in the presence of NOM. A better understanding of the role of shape in the attachment of colloidal particles to environmentally relevant surfaces will lead to a more accurate prediction of colloidal particle transport, aiding in risk assessment of potential exposure pathways.

2. Materials and Methods

2.1. Materials

200 nm carboxylate-modified polystyrene (PS) spheres were purchased from Phosphorex (107, Hopkinton, MA). Dry Harpeth humic acid (HHA) was isolated and characterized as described in our previous publication (DeLapp et al., 2005). Alginic acid sodium salt (alginate, A2158), poly-L-lysine hydrobromide (PLL, P1274), and 4-(2-Hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES) were purchased from Sigma-Aldrich (St. Louis, MO). Reagent grade NaCl (S671) was purchased from Fisher Scientific (Pittsburgh, PA). Silica-coated QCM-D sensors (QSX-303) were purchased from Q-Sense (Biolin Scientific, Stockholm, Sweden). 900 nm silica microspheres were pur-

92 chased from Polysciences Inc (Warrington, PA) as a surrogate for estimating
93 the electrophoretic mobility of the silica sensor surface. All solutions were
94 prepared using ultra pure water purified by the Milli-Q Water Purification
95 System from Millipore (Billerica, MA).

96 *2.2. Preparation of Stretched PS Particles*

97 The particle stretching procedure used in this study is based on a method
98 previously published by Champion et al. (2007) and the details can be found
99 in Appendix A.1. In order to determine the concentration of the stretched
100 particles, a calibration curve was constructed using known concentrations of
101 stock PS particles and UV-vis spectrophotometry (NanoDrop 2000 Thermo
102 Scientific, Wilmington, DE). The resulting calibration curve can be seen in
103 Appendix A.1. The stock stretched PS suspension was determined to have a
104 concentration of 129 mg L⁻¹.

105 *2.3. Preparation of HHA Solution*

106 In order to prepare the HHA solution, 50 mg dry HHA was introduced into
107 400 mL deionized water and stirred for more than 3 hours. During this time,
108 the pH was adjusted drop wise with 0.1 N NaOH to a pH of 10.0 to allow the
109 HHA to dissolve. After nearly complete dissolution of the HHA, the pH was
110 adjusted drop wise with HCl down to 7.0. The alginate stock solution was
111 prepared by stirring 50 mg dry alginate in 400 mL deionized water overnight,
112 after which time the alginate was adjusted drop wise with 0.1 N NaOH to a
113 pH of 7.0. Both HHA and alginate stock solutions were filtered through 0.22
114 μ m pore size membrane filter paper (Fisher, GSWP02500) and kept in the
115 dark for the entirety of the study, during which time they remained stable

116 to aggregation as confirmed by periodic DLS measurements. The resulting
117 HHA and alginate stock solutions were determined to have a total carbon
118 content (Shimadzu TOC-V CPH/CPN, Columbia, MD) of 110 and 102 mg
119 L⁻¹, respectively.

120 All prepared electrolyte solutions were filtered through a 0.22 μ m pore size
121 membrane filter paper and pH adjusted so that all attachment experiments
122 could take place at a pH of 7.0.

123 *2.4. Characterization Measurements*

124 Because particle size can control diffusion rate, DLS (Malvern Zetasizer
125 Nano ZS, Worcestershire, UK) was utilized to measure the size of spherical
126 PS particles at each experimental condition investigated. Five independent
127 runs at 1 minute each were performed for each particle size measurement,
128 with each resulting data point consisting of 5 independent measurements.

129 Image J software was used to measure the length of major and secondary
130 axes of the stretched PS particles. Figs. B.13, B.14, and B.15 show the dis-
131 tribution of major and minor axis of the stretched PS particles and their ratio
132 based on the Image J measurement of 100 particles. Additional shape related
133 parameters including averaged ellipticity, effective diameter, and surface area
134 and the method for calculating these values are provided in Appendix B.

135 Electrophoretic mobility (EPM) measurements were conducted for the
136 spherical and stretched PS particles at each experimental condition by DLS
137 in conjunction with a universal dip cell (Malvern ZEN1002, Worcestershire,
138 UK). Each reported value of EPM was the result of 10 independent measure-
139 ments. In order to estimate the EPM values of the silica depositional surfaces
140 utilized in this study, 900 nm silica microspheres were used as a surrogate.

141 EPM values were measured for uncoated, HHA-coated, and alginate-coated
 142 silica at each experimental condition. In order to coat the silica microspheres,
 143 they were first introduced into a 100 mg L⁻¹ solution of PLL, stirred for 20
 144 minutes and then drained through 0.45 μ m pore size membrane filter paper
 145 (Fisher, GSWP02500) while being rinsed with DI water, allowing all un-
 146 bound PLL to pass through, but leaving the positively charged, PLL-coated
 147 silica particles behind. The process was then repeated for a HHA or alginate
 148 coating. All depositional surface EPM measurements were conducted at a
 149 silica concentration of 10 mg L⁻¹. Zeta potentials were estimated using the
 150 Smoluchowski approximation (Hunter, 2013).

151 *2.5. Attachment Experiments*

152 The deposition rate of spherical or stretched PS was monitored using a
 153 QCM-D (Q-Sense E4 unit, Biolin Scientific, Stockholm, Sweden) under vary-
 154 ing experimental conditions. Flowrates were held constant at 0.1 mL min⁻¹,
 155 resulting in laminar flow within the module as confirmed by a Reynolds
 156 Number of 0.26 (Appendix C). PS particle concentration and pH was held
 157 constant at 6 mg L⁻¹ and 7, respectively, in order to simulate environmen-
 158 tally relevant conditions. All experiments took place at a temperature of 20
 159 °C, which was held constant by a Peltier element. Before each experiment,
 160 the silica QCM-D sensors were soaked in a 2% Hellmanex II solution (Mull-
 161 heim, Germany) overnight, rinsed in DI water, and dried in ultrapure N₂.
 162 The sensors were then cleaned in a UV-Ozone cleaner (Jelight 42, Irvine,
 163 CA) for 20 minutes immediately before being loaded into the QCM-D.

164 A representative QCM-D experiment and detailed experimental protocol
 165 are provided in Appendix A.2. As particles attach to the sensor surface, mass

166 increases, corresponding to a continuous decrease in frequency, as described
 167 in the Sauerbrey relation (Sauerbrey, 1959). The Sauerbrey relation can be
 168 seen in Eq. 1, where m is the mass deposited, C is the crystal constant (17.7
 169 $\text{ng cm}^{-2} \text{ Hz}^{-1}$) and f_n is the frequency at overtone n .

$$\Delta m = -C \frac{1}{n} \Delta f_n \quad (1)$$

170 In order to compare the particle attachment between varying ionic strengths
 171 independent of aggregation and diffusion effects, the deposition attachment
 172 efficiency (α) was calculated from Eq. 2, where df_3/dt is the initial deposition
 173 rate of the third overtone of frequency calculated from the first 120 seconds of
 174 frequency drop and $(df_3/dt)_{diff \text{ limited}}$ is the diffusion limited deposition rate,
 175 under identical experimental conditions. The diffusion limited deposition
 176 rate was measured by flowing the PS particles over the PLL layer at each
 177 experimental condition investigated. Since the PS particles are negatively
 178 charged and the PLL layer is positively charged, there is no energy barrier to
 179 deposition and any PS particles that flow near the PLL surface will attach,
 180 therefore the deposition is limited only by diffusion of the PS particles to the
 181 sensor surface.

$$\alpha = \frac{df_3/dt}{(df_3/dt)_{diff \text{ limited}}} \quad (2)$$

182 2.6. AFM Images

183 A Bruker Dimension Icon AFM (Billerica, MA) was used to image the
 184 HHA and alginate surfaces. The HHA or alginate layer was constructed as
 185 described in the experimental procedure, carefully removed from the QCM-D,

186 dried in N_2 , and loaded into the AFM for imaging. The AFM was operated in
187 tapping mode, using a silicon cantilever. The nominal tip characteristics were
188 8 nm radius of curvature, 40 N m^{-1} spring constant, and 300 kHz resonant
189 frequency.

190 *2.7. DLVO Calculations*

191 The interaction energy between the PS particles and the collector surface
192 was calculated using the surface element integration (SEI) method. SEI is a
193 method for evaluating DLVO interaction energy between a particle and a flat
194 plate (Bhattacharjee and Elimelech, 1997). Unlike the sphere-plate DLVO
195 estimation methods more commonly applied to nanoparticle-plate interactions
196 (Elimelech et al., 2013; Hogg et al., 1966), the SEI method accounts
197 for the orientation dependence of the interaction energy between a flat sur-
198 face and a spheroidal particle (Bhattacharjee and Elimelech, 1997; Wu et al.,
199 2013). Details of the SEI method are provided in Appendix D.

200 **3. Results and Discussion**

201 *3.1. Particle and Surface Characterization*

202 Spherical and stretched PS particles were investigated by SEM (Hitachi
203 S4700) and representative images can be seen in Fig. 1a and 1b, respectively.
204 SEM images of the stretched PS particles were used to quantify the shape
205 of the particles using Image J software. Major axis diameter, minor axis
206 diameter, ratio of axis diameters, ellipticity, surface area, and effective di-
207 ameter were all estimated for both the spherical and stretched PS particles.
208 A summary of the shape quantification along with a detailed explanation of

Figure 1: Representative SEM images of spherical (A) and stretched (B) PS particles.

209 calculation method are provided in Appendix B. After stretching, the major
 210 to minor axis ratio was raised from 1:1 to 1.6:1 and the ellipticity was nearly
 211 doubled.

212 The diameter of spherical PS and EPM of spherical and stretched PS
 213 were measured as a function of ionic strength and can be seen in Fig. 2. The
 214 spherical PS particle diameter was as expected, based on the nominal 200
 215 nm particle size reported by the manufacturer. The spherical PS diameter
 216 remained constant over the ionic strength range investigated, suggesting there
 217 was no significant aggregation of the particles. Particle size distributions at
 218 each NaCl concentration investigated can be found in Appendix B.

219 Both spherical and stretched PS were negatively charged, with the stretched
 220 PS carrying a smaller charge (closer to neutral) throughout the entire ionic
 221 strength range investigated. Several previous studies have reported a change
 222 in EPM between spherical and stretched particles (Seymour et al., 2013; Liu
 223 et al., 2010; Salerno et al., 2006; Ho and Ottewill, 1998; Ho et al., 1997). One
 224 such study (Seymour et al., 2013), using identical particles to those used here,

Figure 2: EPM measurements of spherical and stretched PS and particle diameter of spherical PS. The control value refers to spherical PS which were exposed to an identical experimental routine as the stretched PS, without being stretched. Each value was the result of 10 independent measurements and error bars represent standard deviation.

225 reported that the EPM of PS particles decreased (closer to neutral) as as-
 226 pect ratio increased, therefore the sensitivity of EPM to aspect ratio reported
 227 here is consistent with previous studies. The sensitivity of EPM to aspect
 228 ratio could be a result of altered charge density due to a change in surface
 229 area, or altered surface chemistry due to residual chemicals from the particle
 230 stretching process (Champion et al., 2007). In order to evaluate which of
 231 these possible contributors had a larger effect, a control group of spherical
 232 particles was taken through an identical stretching procedure without being
 233 stretched, exposing the control group to all the same chemicals. As can be
 234 seen in Fig. 2, the EPM of the control particles remained statistically iden-
 235 tical to that of the spherical PS particles, similar to the reported control
 236 in the aforementioned study (Seymour et al., 2013). This suggests that an
 237 altered charge density of the stretched particles is the main contributor to
 238 the EPM sensitivity to aspect ratio observed here and elsewhere. The same
 239 control group was also used in attachment experiments, to further validate
 240 this finding.

241 The EPM of each depositional surface was also measured and reported in
 242 Fig. 3. Each surface was negatively charged throughout the ionic strength
 243 range investigated and the EPM of the HHA and alginate surfaces were
 244 statistically identical at each ionic strength. These findings are in agreement
 245 with previous reports for silica surfaces coated with similar NOM (McNew
 246 and LeBoeuf, 2015; Qu et al., 2012). We observed a positive charge for PLL-
 247 coated silica, validating it's use to obtain the deposition rate of negatively
 248 charged spherical and stretched PS under diffusion-limited conditions (Eq.
 249 2).

Figure 3: EPM measurements of each depositional surface as a function of ionic strength. Each value was the result of 10 independent measurements and error bars represent standard deviation.

250 3.2. Attachment Results

251 For the first time, we report the attachment efficiency of spherical and
252 stretched PS particles onto HHA and alginate coated silica surfaces as a func-
253 tion of ionic strength in Fig. 4. In the presence of the HHA coated silica
254 surface, we observed a higher attachment of spherical than stretched PS at
255 low ionic strengths. At a NaCl concentration of 100 mM, we observed similar
256 attachment values for spherical and stretched PS and above 100 mM NaCl,
257 we observed a higher attachment of stretched than spherical PS. The attach-
258 ment of the spherical PS was not sensitive to NaCl concentration, while the
259 attachment of stretched PS showed a steady increase as NaCl concentration
260 increased. The attachment of the control particles, which were exposed to all
261 the same chemicals as the stretched particles without being stretched, didn't
262 deviate from the attachment of the spherical PS. This confirms that the ob-
263 served differences in attachment between spherical and stretched particles
264 are due to the differences in particle shape, rather than a surface chemistry
265 alteration as a result of exposure to the chemicals required in the stretching
266 procedure. This control group finding is in agreement with several previous
267 studies (Knappenberger et al., 2015; Aramrak et al., 2013; Salerno et al.,
268 2006), including a study by Seymour et al. (2013) which reported similar de-
269 position rates between spherical PS and control particles, despite observing
270 differences for stretched PS. Attachment of spherical and stretched PS onto
271 the alginate coated silica surface, however, were statistically identical for all
272 ionic strengths investigated, except for a small deviation at 30 mM NaCl.

273 Total DLVO interaction energy was calculated using the SEI method
274 (Bhattacharjee and Elimelech, 1997) to account for the orientation depen-

Figure 4: Attachment efficiency of spherical and stretched PS particles onto HHA (a) and alginate (b) coated silica surfaces as a function of ionic strength. Each value was the result of at least 4 independent measurements and error bars represent standard deviation.

Figure 5: Calculated DLVO interaction energy for the deposition of spherical and stretched PS (side on or end on) onto HHA in the presence of 16 (a) and 200 (b) mM NaCl.

275 dence of the interaction energy between a flat surface and a spheroidal par-
 276 ticle. Details of this calculation method can be found in Appendix D. Total
 277 interaction energy for the stretched PS was calculated as the particles ap-
 278 proached the surface in two different orientations: major axis parallel to
 279 the surface (side on) and major axis perpendicular to the surface (end on).
 280 The interaction energy profiles for spherical and stretched PS onto HHA are
 281 presented in Fig. 5 in the presence of 16 (a) and 200 (b) mM NaCl.

282 As ionic strength increased from 16 mM in Fig. 5a to 200 mM in 5b, the
 283 electrical double layer repulsion between the negatively charged PS and HHA
 284 coated surface is suppressed and the predicted energy barrier to deposition
 285 is reduced as a result. The observed attachment trends of stretched PS onto
 286 HHA (Fig. 4a) and both spherical and stretched PS onto alginate (Fig.
 287 4b) are in qualitative agreement with this prediction. At 16 mM NaCl, the
 288 predicted energy barrier to deposition for spherical PS is much larger than

289 that of stretched PS in each particle orientation, due to the less negative
290 (closer to neutral) surface charge of the stretched PS. This is in contradiction
291 to the attachment results presented in Fig. 4a and likely due to surface
292 roughness and steric contributions from the HHA layer, not considered by
293 DLVO theory. Non-DLVO contributions are explored and discussed in detail
294 in the following section.

295 As illustrated in Fig. 5, the energy barrier to deposition for stretched PS
296 is dependent upon particle orientation. In 16 mM NaCl, the energy barrier
297 to deposition for side on orientation is 2.4 times larger than that of the end
298 on orientation. It has been hypothesized (O'Brien and Ward, 1988; Ho and
299 Ottewill, 1998; Loewenberg and Obrien, 1992) that the shape of nonspherical
300 particles will induce a tangential flux of ions near the surface of the particles
301 which, in the case of the rod shaped stretched PS particles, will ultimately
302 result in the accumulation of cations near the ends of the particle. This
303 uneven distribution of surface charge is the cause of the orientation dependent
304 energy barrier observed in Fig. 5. Furthermore, the torques experienced
305 by stretched particles as they turn to energetically favorable positions for
306 attachment can cause a reduction in deposition rates (Seymour et al., 2013).
307 This is discussed in detail in the following section. As the NaCl concentration
308 is increased to 200 mM NaCl, the energy barrier vanishes due to significant
309 charge screening and the results presented in Fig. 5b suggest that a side on
310 particle orientation allows for a larger attractive energy well than an end on
311 orientation. More detailed DLVO interaction energy information is included
312 in Appendix D.

3.3. Surface Topography and Non-DLVO Forces

The observed attachment trends onto HHA and alginate surfaces are widely different from one another, despite the surfaces possessing statistically identical charges (Fig. 3), therefore the observed differences in attachment behavior are likely due to physical differences of the surfaces. In order to investigate the physical aspect further, both HHA and alginate surfaces were explored using AFM and representative images are reported in Fig. 6 a and b, respectively. The topography of the HHA surface is very heterogeneous, with large peaks extended from the surface, and a root mean squared (RMS) roughness of 2.51 ± 1.21 . The topography of the alginate surface is smoother, with much fewer peaks extending from the surface relative to HHA, and a RMS roughness of 0.99 ± 0.26 . The rougher, more extended surface of the HHA layer possesses more voids than the alginate layer, and therefore an increased potential for particle entanglement. The smaller size of the spherical PS particles allow for entanglement in these relatively small voids, while the nearly doubled major axis diameter of the stretched PS hinder particle entanglement within the HHA voids. Furthermore, investigation by the Voigt viscoelastic model (Voinova et al., 1999) estimates that the mass of the HHA layer is more than 5 times larger than the mass of the alginate layer (Fig. B.16). This also suggests that the HHA layer provides a much larger mesh for particle entanglement. These findings are in agreement with two previous studies which reported increased attachment of spherical nC₆₀ onto NOM coated surfaces in the presence of low ionic strength solutions (McNew and LeBoeuf, 2015; Chen and Elimelech, 2008). Particle entanglement, in this manner, is not considered in DLVO theory, and is therefore

Figure 6: Representative AFM images of HHA (a) and alginate (b) coated silica surfaces.

likely the main contributor to the observed deviation from DLVO theory at low ionic strength. The qualitative agreement to DLVO theory illustrated by the attachment onto alginate, along with the AFM images and measured surface roughness of alginate, however, suggest that the alginate layer did not contribute voids suitable for particle entanglement.

Immobilized macromolecule structure has been reported to depend heavily on the ionic strength of solution (Yuan et al., 2008; Hong and Elimelech, 1997). Furthermore, NOM layers have been reported to condense in the presence of high ionic strength solutions (Chen and Elimelech, 2006, 2008). As ionic strength increases, the HHA layer condenses, induced by increased inter- and intra-molecular crosslinks, forming a smoother, less extended sur-

349 face with fewer voids for particle entanglement. Since the condensed surface
 350 has a lower potential for particle entanglement, the particle entanglement ef-
 351 fect seen at low ionic strength diminishes as ionic strength increases. Though
 352 spherical PS particles experience a reduced energy barrier to deposition as
 353 ionic strength increases (Fig. 5), this effect is offset by reduced particle en-
 354 tanglement, induced by HHA layer compaction, leading to no significant net
 355 change in attachment and a spherical PS attachment trend which is rela-
 356 tively insensitive to ionic strength. Since stretched PS particles experience
 357 less particle entanglement due to their enlarged major axis, they are free
 358 to experience the reduced energy barrier and the stretched PS attachment
 359 trend increases with ionic strength, as predicted by DLVO theory. Two pre-
 360 vious studies have reported reduced attachment of spherical particles onto
 361 NOM layers as ionic strength increased (McNew and LeBoeuf, 2015; Chen
 362 and Elimelech, 2008), however none have yet illustrated the dependency on
 363 aspect ratio reported in this study. Though all experiments in this study
 364 were performed in the presence of monovalent salt solutions, in our previous
 365 study (McNew and LeBoeuf, 2015) we reported a similar HHA layer com-
 366 paction in the presence of both mono and divalent cations (Na^+ and Ca^{2+}).
 367 Whether or not this finding extends to variable particle shape, however, is
 368 not yet known.

369 Though stretched PS particles exhibit a lower (closer to neutral) surface
 370 charge (Fig. 2), we observe statistically similar attachment between stretched
 371 and spherical PS onto the smooth alginate layer throughout the ionic strength
 372 range investigated (Fig. 4b). The reason for this deviation from DLVO lies
 373 within the orientation dependent interaction energy of the stretched PS. The

374 stretched PS experience torques to align the particles into an energetically fa-
 375 vorable orientation for deposition (O'brien and Ward, 1988; Ho and Ottewill,
 376 1998; Loewenberg and Obrien, 1992). These rotational forces and induced
 377 direction changes cause the stretched PS particles to follow an oscillatory flow
 378 path with respect to the depositional surface, as observed in several studies
 379 on the flow trajectory of submicrometer, non-spherical particles (Gavze and
 380 Shapiro, 1995; Blaser, 2002; Decuzzi and Ferrari, 2006). The flow path of the
 381 spherical particles within these studies, however, was observed to be parallel
 382 to the surface. In this manner, the larger hydrodynamic forces experienced
 383 by the stretched PS led to a reduction in deposition rate, which resulted in
 384 attachment values comparable to that of the more electrostatically repulsive
 385 spherical PS.

386 *3.4. Interpretation of Energy Dissipation*

387 The dissipation parameter is a dimensionless quantity which can be used
 388 to infer about the viscoelastic properties of the mass coupled to the sensor
 389 (Kananizadeh et al., 2016; Dixon, 2008). Rigid films result in a longer decay
 390 in the oscillatory energy and therefore lower values of the dissipation param-
 391 eter while soft or viscoelastic films result in much faster oscillatory energy
 392 dissipation, due to the poor coupling of the soft material to the stiff sen-
 393 sor, and therefore higher values of the dissipation parameter. Representative
 394 QCM-D deposition data can be seen in Fig. 7 for four different cases: (a)
 395 spherical PS onto PLL, (b) spherical PS onto HHA, (c) stretched PS onto
 396 PLL, and (d) stretched PS onto HHA. All experiments took place in 30 mM
 397 NaCl and overtones 3, 5, 7, 9, 11, and 13 are displayed for both frequency
 398 and dissipation.

Figure 7: Representative QCM-D deposition data for spherical PS onto PLL (a), spherical PS onto HHA (b), stretched PS onto PLL (c), and stretched PS onto HHA (d). All experiments took place in 30 mM NaCl.

399 A significant increase in dissipation was observed ($>5\%$ ΔD) for each case
 400 presented in Fig. 7, suggesting that both spherical and stretched PS particles
 401 attached to each surface in a soft, viscoelastic layer (Kananizadeh et al., 2016;
 402 Reviakine et al., 2011; Dixon, 2008). As the spherical PS attached to the
 403 PLL surface (Fig. 7a), no additional spread in the overtones of dissipation
 404 was observed, suggesting that the particles formed a homogenous, soft layer
 405 (Reviakine et al., 2011; Dixon, 2008). A homogenous layer is expected in
 406 this case, due to the spherical shape of the particles and their resulting
 407 independence upon particle orientation. As the stretched PS attached to the
 408 PLL surface (Fig. 7c) however, a very pronounced spread of the overtones
 409 of dissipation is observed, suggesting the formation of a heterogenous, soft
 410 film. Due to their altered aspect ratio, the stretched PS particles attach
 411 to the surface in various configurations, leading to an increase in surface
 412 heterogeneity and roughness, resulting in a larger dissipation increase and
 413 much larger spread of overtones. As expected for the rougher and more
 414 extended HHA layer, attachment of both spherical (Fig. 7b) and stretched
 415 PS (Fig. 7d) resulted in a heterogeneous, soft layer. Despite attaching at a
 416 lower rate (Fig. 4), the stretched PS resulted in a similar increase and spread
 417 of dissipation overtones. This can again be attributed to the altered aspect
 418 ratio of the stretched particles, resulting in various attachment orientations.

419 4. Conclusions

420 In this study, we showed that the attachment of colloidal particles onto
 421 NOM-coated surfaces can be greatly affected by the shape of the particles, de-
 422 pending on ionic strength and the type of NOM coating. The altered charge

distribution of the stretched PS induced an orientation dependent interaction energy between the particles and the surface, which led to stronger hydrodynamic forces and an oscillatory flow path near the surface, resulting in a reduction in the observed attachment. In the presence of the alginate surface, the attachment of both spherical and stretched PS qualitatively agreed with DLVO theory. In the presence of the HHA surface, however, deviations from DLVO theory were observed. At low ionic strengths, spherical PS attached to HHA at a much higher rate than stretched PS. This deviation from DLVO theory can be explained by the increased surface heterogeneity and roughness observed for the HHA surface. More voids present in the HHA layer allowed for a higher potential of spherical PS particle entanglement, while the enlarged major axis of the stretched particles hindered their ability to become entangled in the extended HHA surface. As ionic strength increased, the HHA layer condensed and the potential for spherical particle entanglement is reduced.

Complex interactions exist between colloidal particles and environmentally relevant surfaces and, based on the findings presented in this study, it is clear that the shape of colloidal particles can play a major role in such interactions. If similarly complex interactions exist for other types of environmentally relevant surfaces, particle shape may greatly affect the environmental fate and transport of colloidal particles. A complete understanding of the role of particle shape will improve the accuracy of colloidal particle transport predictions, aiding in the assessment of risk and potential exposure pathways.

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607 **Appendix A. Detailed Experimental Information**

608 *Appendix A.1. Particle Stretching Details*

609 The method described here is based on a procedure previously published
610 by Champion et al. (2007). First, 10% (wt/vol) polyvinyl alcohol (PVA,
611 Sigma Aldrich) solution was introduced into 80 °C Milli-Q water, and stirred
612 for 30 minutes to achieve complete dissolution of PVA. 100 mg glycerol
613 (Sigma Aldrich) and 2.5 mL of 1% solid content (0.0625% (wt/vol) parti-
614 cle/water) PS spheres were added to the PVA solution. The solution mixture
615 was then poured onto a 12 x 12 cm clean film plate and was set to dry for
616 24 hours to form a thin film. The film was then cut into four pieces and
617 subsequently placed in a stretching apparatus (Fig. A.8). The stretching
618 apparatus was submerged in a 125 °C mineral oil (Fisher Scientific) bath for
619 5 minutes and stretched to a 2:1 ratio. This temperature is close to the glass
620 transition temperature of polystyrene particles, which allows the particles to
621 stretch to the desired ratio. The stretched film was then cooled to room tem-
622 perature and cut from the apparatus. After being cleaned by 100% isopropyl

623 alcohol (IPA, Fisher Scientific) for at least two hours, the film was dissolved
624 in 70 °C water for several hours. Finally, the stretched PS particles were
625 cleaned with IPA and extracted using a series of centrifugation (Eppendorf
626 Centrifuge 5840R).

Figure A.8: Diagram of the particle stretching apparatus before (a) and after (b) stretching.

Figure A.9: Calibration curve used in the determination of particle concentration following the stretching procedure.

627 Appendix A.2. QCM-D Experimental Protocol

628 A representative QCM-D experiment is presented in Fig. A.10. A baseline
629 was first collected in a HEPES solution (10 mM HEPES, 100 mM NaCl).
630 The signal was considered stable when the third overtone of frequency (f_3)
631 failed to drift more than 0.3 Hz over the course of 10 minutes. Then, a layer
632 of positively charged PLL was constructed on the silica surface by flowing
633 a solution of 0.1 g L⁻¹ PLL, 10 mM HEPES, and 100 mM NaCl until the
634 signal stabilized. The PLL layer was then washed in the HEPES solution
635 to remove any unbound PLL from the surface. A 1 mM NaCl solution was
636 then introduced until a stable signal was reached, followed by a 0.1 g L⁻¹
637 HHA or alginate solution containing 1 mM NaCl. The negatively charged
638 HHA or alginate readily adsorbed to the oppositely charged PLL surface,
639 forming a second layer. Once the signal stabilized, the HHA or alginate

640 layer was washed in 1 mM NaCl to remove any unbound particles and then
641 a solution of the ionic strength of interest was introduced. Once the signal
642 stabilized, the stock suspension of spherical or stretched PS was diluted to 6
643 mg L⁻¹ with a measured amount of concentrated NaCl solution to form the
644 same ionic strength and then immediately introduced into the measurement
645 chamber. As the PS suspension flowed across the sensor surface, the first 120
646 seconds of the drop in the third overtone of frequency were used to calculate
647 the initial deposition rates for each set of experimental conditions.

Figure A.10: Representative attachment experiment. A baseline is collected in HEPES (A) before PLL is adsorbed to the surface (B), followed by a rinse in HEPES (C). 1 mM NaCl is introduced (D) before HHA or alginate is adsorbed to the surface (E) and rinsed with 1 mM NaCl (F). Finally, the ionic strength of interest is introduced (G) and once a baseline is reached, stretched or spherical PS particles are introduced in a solution of the same ionic strength (H). The third overtone of frequency is displayed.

Figure A.11: The deposition rates of spherical and stretched PS onto bare (a), HHA-coated (b), and alginate-coated (c) silica at each NaCl concentration investigated.

649 **Appendix B. Detailed Characterization Information**

Figure B.12: Particle size distributions of spherical PS at each NaCl concentration investigated, determined by DLS.

Figure B.13: Summary of the major axis dimensions of stretched PS.

Figure B.14: Summary of the minor axis dimensions of stretched PS.

Figure B.15: Summary of the major to minor axis ratios of stretched PS.

Table B.1: Detailed characteristics of spherical and stretched PS particles.

Particle Characteristic	Spherical (Unstretched) PS Particles	Sretched (2:1) PS Particles
Major axis diameter (nm)	208 ± 3	278 ± 13
Minor axis diameter (nm)	190 ± 3	175 ± 5
Ellipticity	0.37 ± 0.04	0.72 ± 0.03
Surface area (μm^2)	0.120 ± 0.003	0.138 ± 0.008
Effective diameter (nm)	196 ± 0.001	208 ± 0.003

650 The ellipticity (e), surface area (S), and effective diameter (d_{eff}) of the
651 rod shape stretched particles are calculated using the following equations,
652 where s and m are the radius of minor and major axis dimensions, respec-
653 tively.

$$e = \sqrt{1 - \frac{s^2}{m^2}} \quad (\text{B.1})$$

$$S = 2\pi s^2 + \frac{2\pi sm}{e} \sin^{-1} e \quad (\text{B.2})$$

$$d_{eff} = 2\sqrt{\frac{s}{4\pi}} \quad (\text{B.3})$$

Figure B.16: The mass of HHA and alginate layers as estimated by the Voigt viscoelastic model, plotted against the relative frequency of NOM layer deposition.

654 Appendix C. Reynolds Number Calculation

655 In order to calculate the Reynolds number (Re) of the QCM-D system, a
656 parallel-plate channel configuration was assumed Elimelech et al. (1998).

$$Re = \frac{\rho v L}{\mu} \quad (C.1)$$

657 Eq. C.1 was used to calculate the Re of the QCM-D system where ρ is the
658 density of water, v is the flow velocity within the chamber ($2 \times 10^{-4} \text{ ms}^{-1}$), L
659 is the half depth of the channel ($3.2 \times 10^{-4} \text{ m}$), and μ is the viscosity of water.

660 Appendix D. DLVO Calculation Details

661 The interaction energy between the stretched nanoparticles and the col-
662 lector surface was measured using surface element integration (SEI) method.
663 SEI is a method for evaluating DLVO interaction between a particle and a
664 flat plate Bhattacharjee and Elimelech (1997). This method accounts for
665 the orientation dependence of the interaction energy between a flat surface
666 and a spheroidal particle by defining the total interaction energy as follows
667 Bhattacharjee and Elimelech (1997); Wu et al. (2013):

$$U(h) = \int_0^{2\pi} \int_0^\pi \vec{n} \cdot \vec{k} [E_{edl}(h) + E_{vdw}(h)] r^2 \sin(\theta) d\theta d\phi \quad (D.1)$$

668 Here $\vec{n}$ is the unit outward normal to the surface element, $\vec{k}$ is the unit
669 normal to the xy plane and directed along positive z-axis. r , θ , and ϕ repre-
670 sent the radial and angular coordinates in the spherical coordinate system.
671 $E_{edl}(h)$ and $E_{vdw}(h)$ define the electrostatic double layer and van der Waals
672 interaction energy per unit area between two planar surfaces positioned at

673 distance h , respectively. Stretched particles can be oriented either side on
 674 or end on. For the side on attachment between stretched particles and flat
 675 surface, the major axis position is parallel to the planar surface, however,
 676 for the end on attachment this axis is perpendicular to the collector surface
 677 plane. These two different configurations were used in the SEI method to
 678 calculate DLVO interaction energy between the stretched nanoparticles and
 679 collector surface.

680 The van der Waals interaction energy and electrostatic double layer in-
 681 teraction energy per unit area for two infinite planar surfaces separated by a
 682 distance h were measured using the method by Elimelech et al. (2013) and
 683 Hogg et al. (1966), respectively:

$$E_{vdw}(h) = \frac{-A}{12\pi h^2} \quad (\text{D.2})$$

$$E_{edl}(h) = \frac{\epsilon_0 \epsilon_r k}{2} (\varphi_s^2 + \varphi_p^2) \left(1 - \coth(kh) + \frac{2\varphi_s \varphi_p}{\varphi_s^2 + \varphi_p^2} \operatorname{cosech}(kh) \right) \quad (\text{D.3})$$

$$k^{-1} = \left(\frac{\epsilon_0 \epsilon_r K_B T}{2e^2 1000 I_c N_A} \right)^{0.5} \quad (\text{D.4})$$

684 Here A is the Hamaker constant (1×10^{-20} J), ϵ_0 (8.85×10^{-12} C²J⁻¹M⁻¹)
 685 and ϵ_r (80.1) are the permittivity of vacuum and relative permittivity of
 686 medium, respectively. φ_p and φ_s are the surface potential of ellipsoidal par-
 687 ticle and collector surface, respectively. k is the inverse Debye length, K_B is
 688 the Boltzmann constant (1.3806×10^{-23} JK⁻¹), T is the temperature (293 K),
 689 I_c is the ionic strength of the nanoparticle suspension (M), N_A is Avogadro's
 690 number (6.02×10^{23}), and e is the elementary charge (1.6×10^{-19} C).

Figure D.17: Calculated DLVO interaction energy profiles between spherical PS and bare, HHA-coated, and alginate-coated silica surfaces in the presence of 16 mM (a), 30 mM (b), 55 mM (c), 100 mM (d), and 200 mM (e) NaCl.

Figure D.18: Calculated DLVO interaction energy profiles between stretched PS and bare, HHA-coated, and alginate-coated silica surfaces in the presence of 16 mM (a), 30 mM (b), 55 mM (c), 100 mM (d), and 200 mM (e) NaCl. Total interaction energy for the stretched PS was calculated as the particles approached the surface in two different orientations: major axis parallel to the surface (side on) and major axis perpendicular to the surface (end on).