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Scott A. Bradford  
USDA-ARS, Scott.Bradford@ars.usda.gov

Hyunjung Kim  
Chonbuk National University

Chongyang Shen  
China Agricultural University

Salini Sasidharan  
University of California, Riverside

Jianying Shang  
China Agricultural University

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Contributions of Nanoscale Roughness to Anomalous Colloid Retention and Stability Behavior

Scott A. Bradford,* Hyunjung Kim,‡ Chongyang Shen,§ Salini Sasidharan,∥ and Jianying Shang§

US Salinity Laboratory, USDA, ARS, Riverside, California 92507, United States
‡Department of Mineral Resources and Energy Engineering, Chonbuk National University, 664-14 Duckjin, Jeonju, Jeonbuk 561-756, Republic of Korea
§Department of Soil and Water Sciences, China Agricultural University, Beijing, China 100193
∥Department of Environmental Sciences, University of California, Riverside, California 92521, United States

Supporting Information

ABSTRACT: All natural surfaces exhibit nanoscale roughness (NR) and chemical heterogeneity (CH) to some extent. Expressions were developed to determine the mean interaction energy between a colloid and a solid−water interface, as well as for colloid−colloid interactions, when both surfaces contain binary NR and CH. The influence of heterogeneity type, roughness parameters, solution ionic strength (IS), mean zeta potential, and colloid size on predicted interaction energy profiles was then investigated. The role of CH was enhanced on smooth surfaces with larger amounts of CH, especially for smaller colloids and higher IS. However, predicted interaction energy profiles were mainly dominated by NR, which tended to lower the energy barrier height and the magnitudes of both the secondary and primary minima, especially when the roughness fraction was small. This dramatically increased the relative importance of primary to secondary minima interactions on net electrostatically unfavorable surfaces, especially when roughness occurred on both surfaces and for conditions that produced small energy barriers (e.g., higher IS, lower pH, lower magnitudes in the zeta potential, and for smaller colloid sizes) on smooth surfaces. The combined influence of roughness and Born repulsion frequently produced a shallow primary minimum that was susceptible to diffusive removal by random variations in kinetic energy, even under electrostatically favorable conditions. Calculations using measured zeta potentials and hypothetical roughness properties demonstrated that roughness provided a viable alternative explanation for many experimental deviations that have previously been attributed to electrosteric repulsion (e.g., a decrease in colloid retention with an increase in solution IS; reversible colloid retention under favorable conditions; and diminished colloid retention and enhanced colloid stability due to adsorbed surfactants, polymers, and/or humic materials).

INTRODUCTION

An understanding of factors that influence interactions of colloids with solid surfaces in the presence of water is needed for many industrial and environmental applications, including: the design of surfaces to enhance or diminish colloid retention, wastewater treatment, remediation of hazardous waste sites, risk assessment of pathogenic microorganisms and engineered nanoparticles, colloid-facilitated contaminant transport, petroleum production, and managed aquifer storage and recovery. Conventional filtration theory considers that the retention rate coefficient depends on the mass transfer and immobilization of colloids on the solid surface. Colloid immobilization has commonly been assumed to be controlled by the adhesive interaction between a colloid and a solid−water interface (SWI). Similarly, the adhesive interaction between colloids determines the stability of a suspension.

The adhesive interaction is commonly derived from interaction energy calculations that consider electrostatic double layer and van der Waals interactions, but may also be extended to include short-range interactions such as Born repulsion, steric, and Lewis acid−base interactions that are still incompletely understood. Colloid and natural surfaces always exhibit some degree of nanoscale roughness (NR) and chemical heterogeneity (CH), and interaction energy calculations based on homogeneous surfaces have frequently been shown to provide an inadequate description of colloid retention on the SWI or colloid stability. A number of researchers have modified interaction energy calculations to account for NR and/or CH on surfaces in order to overcome these limitations. For example, the surface element integration approach allows for the consideration of NR and/or CH on the SWI or the colloid. Results have demonstrated that the mean interaction energy on a heterogeneous surface can be represented as a linear expression of interactions...
energies associated with the various heterogeneity combinations within the electrostatic zone of influence.\textsuperscript{15,16,22} For example, Bradford and Torkzaban\textsuperscript{22} demonstrated that the influence of binary NR and CH on the SWI could be accurately accounted for using a linear expression of the various interaction energies.

Nanoscale heterogeneities have been shown to have a large influence on predicted interaction energy profiles.\textsuperscript{14–25} In brief, electrostatically unfavorable surfaces can exhibit localized reductions and/or elimination of the energy barrier due to the presence of nanoscale heterogeneity in zeta potential, depending on the amount, size, and charge of the CH within the electrostatic zone of influence, the solution ionic strength (IS), and the colloid size.\textsuperscript{16,23} In general, the influence of a given CH increases at higher IS and for smaller colloid size.\textsuperscript{23} The energy barrier on electrostatically unfavorable surfaces can also be locally reduced or eliminated by NR.\textsuperscript{14–22} In addition, the depths of the secondary and primary minima can also be reduced by NR depending on the amount, size, and height of the NR within the electrostatic zone of influence.\textsuperscript{22} Some interacting colloids are therefore susceptible to diffusive and/or hydrodynamic removal on rough surfaces,\textsuperscript{3,4} even under electrostatically favorable conditions.\textsuperscript{25} When both NR and CH are considered on the SWI, results indicate that NR tends to control the interaction energy profile shape, as well as colloid retention and release.\textsuperscript{16,22,24}

To date, no published studies have considered the influence of NR and CH on both the SWI and the colloid. Consequently, it is presently unclear whether heterogeneity needs to be considered only on the SWI, only on the colloid, or on both the SWI and colloid. Furthermore, the predicted influence of NR on interaction energy profiles depends not only on roughness parameters, but also on parameters that influence electrostatic and van der Waals interactions.\textsuperscript{16,22} However, the coupled influence of NR and interaction energy (e.g., zeta potentials, solution chemistry, and colloid size) parameters has not yet been systematically studied when heterogeneity occurs on both the colloid and the SWI. Consideration of these effects may provide a viable alternative explanation for experimental observations that have typically been attributed to electrostatic repulsion.\textsuperscript{26–32} For example, electrostatic repulsion has been invoked to explain: (i) a decrease in colloid retention with an increase in solution IS;\textsuperscript{26,27} (ii) reversible colloid retention under favorable conditions;\textsuperscript{16,29} (iii) diminished colloid retention due to adsorbed humic materials;\textsuperscript{30} and (iv) enhance stability of colloid suspensions by adsorbed polymers and surfactants.\textsuperscript{31,32} However, this literature has not explicitly considered the role of NR on the SWI or the colloid in their interaction energy calculations.

In this work we present simple linear expressions to control the interaction energy profile shape, as well as colloid retention and release.\textsuperscript{16,22,24}

\[ \Phi(h) = a_1 \Phi_1(h + h_r + h_n) + a_2 \Phi_2(h + h_r) + a_3 \Phi_3(h + h_r + h_n) + a_4 \Phi_4(h) \]  

(1)

where \( h \) [L] is the separation distance from the center of \( A_c \) at a height \( h_r \) from the SWI to the leading face of the colloid center at a height \( h_n \) (see Figure 1), \( \Phi_i \) is the dimensionless interaction energy associated with a smooth, nanoscale chemically heterogeneous surface, and \( a_{i1} \), \( a_{i2} \), \( a_{i3} \), and \( a_{i4} \) are constants that determine the contributions of the various possible roughness combinations (e.g., smooth SWI and smooth colloid, smooth SWI and rough colloid, rough SWI and smooth colloid, rough SWI and rough colloid, respectively) that are equal to

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\[ \text{Langmuir 2017, 33, 10094–10105} \]
where $c$ is a critical threshold for long-term colloid immobilization and $H_j$ is a Heaviside function. The value of $H_j = 1$ when the quantity in parentheses is greater than or equal to 0, and $H_j = 0$ when this quantity is less than 0. In this work we have selected $e_1 = 0.01$ to correspond to a magnitude of an interaction energy to enter and escape from a minimum of less than 5.6 (cf. Figure S1). A value of $e_1 > 0$ and $\beta_j = 0$ indicates reversible retention, whereas $e_1 > 0$ and $\beta_j = 1$ denotes irreversible retention for a given solution chemistry condition. It should be mentioned that Eqs 5 and 6 only consider the influence of adhesion and diffusion on colloid immobilization. The role of hydrodynamics on colloid immobilization and the heterogeneous spatial distributions of NR and CH parameters may also be incorporated in this framework, but was not the focus of this study.

**Numerical Experiments.** Numerical experiments were conducted to explore the influence of NR and CH parameters, colloid size, and solution IS on interaction energy profile properties ($\Phi_{min}$, $\Phi_{max}$, and $\Phi_{H_j}$) and probabilities for immobilization ($e_j$ and $e_j^*$), release ($e_j$ and $e_j^*$), and long-term immobilization ($\beta_j$ and $\beta_j$). Two important microbial pathogens were considered in these calculations, namely, *Cryptosporidium oocysts* and *E. coli* O157:H7. Oocysts are approximately spherical, with a diameter that ranges between 3000 and 6000 nm. A sphere-plate interaction was considered between a 4300 nm oocyst and ultrapure quartz sand. *E. coli* O157:H7 is a rod shaped Gram-negative bacterium, and the interaction energy will therefore also depend on the orientation of cell with the SWI. However, available research indicates that a sphere-plate geometry may be used to approximate the interaction between *E. coli* O157:H7 and ultrapure quartz when using an effective cell radius of 720 nm. Hypothetical biocolloids of 100, 1000, and 5000 nm diameters were also employed to study the influence of colloid size. A Hamaker constant of $6.5 \times 10^{-21}$ J was employed to be consistent with reported values for biocolloids. The collision diameter was set equal to 0.26 nm in order to achieve a primary minimum depth at 0.157 nm, a commonly accepted distance of closest approach. Zeta potentials for oocysts, cells, and ultrapure quartz sand at selected solution chemistry conditions were taken directly from the literature, whereas the zeta potential values for the hypothetical biocolloids were assumed to be the same as oocysts or set to $-10$ mV.

A wide range of hypothetical NR parameters on the SWI and colloids were considered in numerical experiments to be consistent with expected variability on natural surfaces. For example, Han et al. measured the roughness of ultrapure quartz sand using atomic force microscopy, and reported a root-mean-square value of $h_{ys} = 33$ nm. This value was quite similar to the value of $h_{ys} = 38$ nm that was reported by Rasmussen et al. for a glass microscope slide that was cleaned with sodium hydroxide. These authors also reported that the maximum valley depths and peak roughness heights were approximately a factor of 5 times the root-mean-square roughness. Atomic force microscopy measurements of the oocyst surface indicates the presence of largest asperities are on the order of 250 nm in diameter and up to approximately 55 nm high. The root-mean-square roughness over micrometer-sized areas on oocysts was found to be in the range from 5 to 20 nm. Imaging of various bacteria species using...
ΦmV) lowers ΦmV). Large values of −minimum (oocyst immobilization exclusively occurred in a secondary CH-Both (continued to dominate immobilization. Inclusion of NR on the adsorption of metal oxides and clays on the SWI.13,51,52 The CH cations; positively charged functional groups on biocolloids; and interaction.

net electrostatically unfavorable conditions exist in this case (when the IS = 10 mM NaCl. Net electrostatically unfavorable conditions were varied from 0.01 to 1. Table 1summarizes the experimental conditions and NR (cr) and CH (sr) parameters used in interaction energy calculations. Roughness parameters on the colloid and SWI were chosen to be the same (e.g., cr = cr and cr = cr) in NR-Both and CH+NR-Both calculations in order to minimize the number of considered roughness parameters. Justification for this choice will be given below.

RESULTS AND DISCUSSION

Figure 2 presents the interaction energy profile between an oocyst and quartz sand for the indicated NR and CH conditions when the IS = 10 mM NaCl. Parameter values are summarized in Table 1.

SWI (fr = 0.05 and hSw = 25 nm) or the colloid (fr = 0.05 and hSw = 25 nm) produced identical interaction energy profiles, with Fmin = −2.06, Fmax = 1.82, and F1min = −454. This observation indicates that changes in hSw or hSw produced a similar influence on the interaction energy profile. Comparison of interaction energy profiles for H-Both, NR-SWI, and NR-Colloid indicates that NR significantly decreased the

Table 1. Summary of Experimental Conditions and NR and CH Parameters for the Numerical Experiments

<table>
<thead>
<tr>
<th>Figure</th>
<th>model</th>
<th>d [nm]</th>
<th>IS [mM]</th>
<th>ζcr [mV]</th>
<th>ζsr [mV]</th>
<th>fcr [-]</th>
<th>ζs+ [-]</th>
<th>hSw [nm]</th>
<th>fr [-]</th>
</tr>
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<td>a</td>
<td>4300</td>
<td>10</td>
<td>−61.8</td>
<td>−6.0</td>
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<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>2</td>
<td>b</td>
<td>4300</td>
<td>10</td>
<td>−61.8</td>
<td>−6.0</td>
<td>10.0</td>
<td>0.025</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>2</td>
<td>c</td>
<td>4300</td>
<td>10</td>
<td>−61.8</td>
<td>−6.0</td>
<td>10.0</td>
<td>0.025</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>2</td>
<td>d</td>
<td>4300</td>
<td>10</td>
<td>−61.8</td>
<td>−6.0</td>
<td>10.0</td>
<td>0.025</td>
<td>0.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

3A     | b     | 4300  | 10     | −61.8    | −6.0     | 10.0   | 0.025    | 0.0      | 0.0    |
| 3A     | c     | 4300  | 10     | −61.8    | −6.0     | 10.0   | 0.025    | 0.0      | 0.0    |
| 3A     | e     | 4300  | 10     | −61.8    | −6.0     | 10.0   | 0.025    | 0.0      | 0.0    |
| 3A     | f     | 4300  | 10     | −61.8    | −6.0     | 10.0   | 0.025    | 0.0      | 0.0    |
| 3B     | b     | 4300  | 10     | −61.8    | −6.0     | 10.0   | 0.025    | 0.0      | 0.0    |
| 3B     | c     | 4300  | 10     | −61.8    | −6.0     | 10.0   | 0.025    | 0.0      | 0.0    |
| 3B     | e     | 4300  | 10     | −61.8    | −6.0     | 10.0   | 0.025    | 0.0      | 0.0    |
| 4, 5   | f     | 4300  | 10     | −61.8    | −6.0     | 10.0   | 0.025    | 10.0    |
| 6      | b     | 1000  | 10     | −61.8    | −6.0     | 10.0   | 0.025    | 0.0      | 0.0    |
| 7A     | c     | 4300  | 10     | −61.8    | −6.0     | 0.0    | 0.0      | 0.0      | 0.0    |
| 7B     | c     | 4300  | 10     | −61.8    | −6.0     | 0.0    | 0.0      | 0.0      | 0.0    |
| 7C     | c     | 4300  | 1000   | −17.3    | −6.6     | 0.0    | 0.0      | 0.0      | 0.0    |
| 8A     | c     | 720   | 1      | −63.8    | −2.1     | 0.0    | 0.0      | 0.0      | 0.0    |
| 8B     | c     | 720   | 10     | −53.5    | −2.1     | 0.0    | 0.0      | 0.0      | 0.0    |
| 8C     | c     | 720   | 1000   | −29.8    | −5.9     | 0.0    | 0.0      | 0.0      | 0.0    |
| 9A     | g     | 1000  | 10     | −10.0    | −10.0    | 0.0    | 0.0      | 0.0      | 0.0    |
| 9B     | g     | 1000  | 1000   | −10.0    | −10.0    | 0.0    | 0.0      | 0.0      | 0.0    |
| 9C     | g     | 5000  | 1000   | −10.0    | −10.0    | 0.0    | 0.0      | 0.0      | 0.0    |

Denotes H-Both with sphere–plate interaction. Denotes CH-Both with sphere–plate interaction. Denotes NR-SWI with sphere–plate interaction. Denotes NR-Colloid with sphere–plate interaction. Denotes NR-Both with sphere–plate interaction. Denotes NR-Both with sphere–sphere interaction. Denotes hSw = hSw, and values were varied from 0 to 80 nm. Denotes fr = fr, and values were varied from 0.01 to 1.
magnitudes of $\Phi_{\text{min}}$, $\Phi_{\text{max}}$ and $\Phi_{1\text{min}}$ such that the relative importance of the secondary minimum was decreased ($\epsilon_1$ from 0.98 to 0.75) and the primary minimum increased ($\epsilon_2$ from 0 to 0.05). These results are consistent with previous literature findings.\textsuperscript{14–22} Interestingly, consideration of NR on both the oocyst and SWI ($f_u = 0.025, h_u = 12.5$ nm, $f_s = 0.025$, and $h_s = 12.5$ nm) altogether eliminated $\Phi_{1\text{min}}$ and $\Phi_{\text{max}}$ and produced a relatively shallow $\Phi_{\text{min}} = -9.5$. In this case, immobilization was exclusively controlled by the primary minimum and the values of $\epsilon_1 = 1.0$ and $\epsilon_2 = 0.0$. The value of $\Phi_{\text{max}}$ was lowered, the magnitude of $\Phi_{1\text{min}}$ decreased, and therefore $\epsilon_1$ increased for NR-Both ($f_u = f_s = 0.025$) compared to NR-Colloid ($f_u = 0$ and $f_s = 0.05$) and NR-SWI ($f_u = 0.05$ and $f_s = 0$) due to differences in $f_u$ and $f_s$. Results from the NR-Both and CH+NR-Both conditions were nearly identical, and this indicates that NR controlled the properties of these interaction energy profiles for the considered heterogeneity parameters. Previous literature\textsuperscript{14–22} has not considered the influence of NR on both the SWI and the colloids, and these calculations clearly demonstrate that inclusion of NR on both the SWI and the colloid has a large influence on the interaction energy profile and the probability for immobilization under electrostatically unfavorable conditions.

Additional interaction energy calculations were conducted to better elucidate the relative importance of CH and NR over a wider range of conditions. Figure 3 presents interaction energy profiles for the CH-Both (A) and CH+NR-Both (B) conditions when $f_s$ was equal to 0.0, 0.25, 0.5, 0.75, and 1.0 and other NR and CH parameters were the same as in Figure 2 (Table 1).

Figure 3. Dimensionless interaction energy profiles for the CH-Both (A) and CH+NR-Both (B) conditions when $f_s$ was equal to 0.0, 0.25, 0.5, 0.75, and 1.0 and other NR and CH parameters were the same as in Figure 2 (Table 1).

sensitivity to changes in $f_u$ from 0 to 1 when NR was included (Figure 3B). The value of $\Phi_{\text{max}}$ was always eliminated, and $\Phi_{1\text{min}}$ was shallow ($> -10$). Although CH parameters played an important role in interaction energy profiles in the absence of NR (Figure 3A), Figure 3B clearly indicates that NR parameters controlled the interaction energy profiles in the CH+NR-Both calculations, even under electrostatically favorable conditions. These results are consistent with previous literature that has examined the influence of CH and NR on the SWI\textsuperscript{22,24} but now CH has an even smaller influence on interaction energy parameters and colloid retention when NR occurs on both the SWI and colloid.

In addition to roughness, the depth of $\Phi_{1\text{min}}$ is also a function of the zeta potential and CH parameters. Figure S2 presents a plot of $\Phi_{1\text{min}}$ for an oocyst when the IS = 10 mM and the zeta potential of the oocyst and the SWI were varied between −60 to 60 mV. Positive values of $\Phi_{1\text{min}}$ were obtained under highly repulsive electrostatic interactions (e.g., highly negative or positive values of both zeta potentials), whereas $\Phi_{1\text{min}}$ decreased and became more negative as the electrostatic interaction became more attractive (e.g., the difference in the zeta potentials increased). The electrostatic interaction goes to zero as the zeta potentials of both the oocyst and SWI approach zero. An increase in $f_u$ from 0 to 1 actually produced a decrease in magnitude of $\Phi_{1\text{min}}$ in Figures 3A and 3B due to the near neutral value of $\zeta_{\text{oocyst}}$ (−6 mV) which produced a more attractive electrostatic interaction with $\zeta_{\text{SWI}}$ (−61.7 mV) than with $\zeta_{\text{oocyst}}$ (10 mV). If $\zeta_{\text{oocyst}}$ is more negatively charged or $\zeta_{\text{SWI}}$ is more positively charged, then $\Phi_{1\text{min}}$ and $\Phi_{\text{max}}$ will decrease with increasing $f_u$ as expected.$^53$

Figure 4 shows contour plots of $\Phi_{1\text{min}}$ (Figure 4A), $\Phi_{\text{max}}$ (Figure 4B), and $\Phi_{\text{max}}$ (Figure 4C) for an oocyst and quartz sand for the CH+NR-Both condition when the IS = 10 mM NaCl. Parameter values were the same as in Figure 2 (Table 1), with the exception that $f_u = f_s$ was now varied between 0.01 and 1 and $h_u = h_s$ ranged from 0 to 80 nm. Note that interaction energy profile parameters were very sensitive to the roughness height and fraction. Primary minimum interactions were possible when $f_u = f_s = \leq 0.25$ and $h_u = h_s \geq 10$ nm because $\Phi_{\text{max}}$ was less than 5. In this case, the $f_u = f_s$ had a greater influence on the interaction energy parameters than $h_u = h_s$. For example, the value of $\Phi_{1\text{min}}$ became shallower with further decreases in $f_u = f_s$. The value of $\Phi_{\text{max}}$ significantly increased when $f_u = f_s > 0.25$, such that the oocyst interaction was mainly limited to the secondary minimum, which became shallower for smaller $f_u = f_s$. The insensitivity of interaction energy parameters on $h_u = h_s \geq 10$ nm is because the bulk colloid and collector surfaces receded very far, which had little influence on the total interaction energy. Similar to Figure 3B, variations in CH parameters were found to have a greater influence on interaction energy parameters when $f_u = f_s > 0.25$ (data not shown).

An alternative way of examining the roles of NR and CH on colloid immobilization is to present the energy balance results in terms of $\epsilon_1, \epsilon_2, \beta_1$, and $\beta_2$. For example, interaction energy parameters shown in Figure 4 were utilized in eqs 5 and 6 to determine $\epsilon_1, \epsilon_2, \beta_1$, and $\beta_2$. Shown in Figure 5 as a function of $f_u = f_s$ and of $h_u = h_s$. Consistent with Figure 4, $\epsilon_1 > 0$ occurred when $f_u = f_s \geq 0.25$ and $h_u = h_s \geq 10$ nm, whereas $\epsilon_2 > 0$ dominated oocyst immobilization for the opposite roughness conditions. Interestingly, values of $\beta_1$ were always zero and this indicates that oocyst interaction in the secondary minimum was always reversible. In contrast, some values of $\beta_1$ were
irreversible for the selected solution chemistry under certain roughness conditions. In particular, values of $\beta_1 = 1$ when $0.025 \leq f_{sr} = f_{cr} \leq 0.25$ and $h_{sr} = h_{cr} \geq 10$ nm. It should be mentioned that eq 6 can be modified to incorporate the influence of flowing water on the torque balance and spatial variations in NR and CH heterogeneity parameters on the SWI. Consequently, this information can be used to design surfaces with specific roughness characteristics for reversible or irreversible colloids retention under selected physicochemical conditions, or to study colloid retention and release on natural heterogeneous surfaces.

The electrostatic double layer and van der Waals interactions are proportional to the colloid radius (eqs S2 and S3). Consequently, if other parameter values remain unchanged, then the magnitudes of $\Phi_{1\text{min}}, \Phi_{\text{max}}$, and $\Phi_{2\text{min}}$ will decrease with decreasing colloid size. This information implies that the influence of NR and CH on interaction energy parameters is enhanced for small colloid sizes. To illustrate this point Figure 6 presents contour plots of $\varepsilon_1$ and $\beta_1$ for a 100 nm colloid as a function of $f_{sr} = f_{cr}$ and $h_{sr} = h_{cr}$ for the same conditions shown in Figure 5. In comparison to Figure 5, values of $\varepsilon_1 > 0$ and $\beta_1 = 1$ now occur over a wider range of roughness conditions. In particular, values of $\beta_1 = 1$ occurred when $f_{sr} = f_{cr} \geq 0.25$ and $h_{sr} = h_{cr} \geq 2.5$ nm. Reversible primary and secondary minimum interactions were predicted when the IS = 10 mM when $f_{sr} = f_{cr} < 0.25$. Consequently, high mobility of nanoparticles is expected in systems with certain roughness conditions (low values of $f_{sr}$ and $f_{cr}$), but not for others. This finding is consistent with experimental observations for viruses.

Input parameters for the electrostatic double layer interaction are strong functions of the solution chemistry. For example, changes in the solution IS are known to alter both the double layer thickness and the zeta potentials. Additional calculations were therefore performed to assess the influence of NR parameters on oocyst retention when the IS = 1, 10, and 100 mM. All secondary minimum interactions were reversible, whereas primary minimum interactions were reversible or irreversible depending on the influence that roughness parameters had on $\Phi_{\text{max}}$ and $\Phi_{1\text{min}}$. Figure 7 summarizes this information by presenting contour plots of $\beta_1$ for the oocysts as a function of $f_{sr} = f_{cr}$ (ranged from 0.01 to 1) and $h_{sr} = h_{cr}$ (ranged from 0 to 80 nm) for the various IS conditions. A wider range in roughness parameters contributes to irreversible oocyst interaction ($\beta_1 = 1$) as the IS increases due to compression of the double layer thickness and a reduction in $\Phi_{\text{max}}$. This produces an increase in colloid retention with IS that has been experimentally observed. However, some roughness conditions still produced reversible interaction ($\beta_1 = 0$) in the absence of $\Phi_{\text{max}}$ when the IS = 100 mM because of the presence of a shallow $\Phi_{1\text{min}}$ that was susceptible to diffusive oocyst release. Consequently, only a fraction of the solid surface area may contribute to oocyst immobilization even in the absence of an energy barrier. This observation has been experimentally and theoretically confirmed previously. Interestingly, some roughness conditions (e.g., $0.025 \leq f_{sr} = f_{cr}$...
≤ 0.05 and $h_{sr} = h_{cr} \geq 10$ nm) transferred from irreversible to reversible interaction as the IS increased from 10 to 100 mM because the magnitude of $\Phi_{1\min}$ decreased with compression of the double layer thickness. This issue will be further investigated subsequently.

Kim et al.\textsuperscript{26} observed a pronounced decrease in *E. coli* O157:H7 retention with an increase in solution IS. This trend is not consistent with interaction energy calculations for a homogeneous cell and SWI, and it has therefore been attributed to electrostatic repulsion.\textsuperscript{26} Interaction energy profiles between *E. coli* O157:H7 and quartz sand when the IS = 1, 10, and 100 mM NaCl were determined over a range in $f_{sr} = f_{cr}$ (0.01−1) and $h_{sr} = h_{cr}$ (0−80) conditions to see if NR provides a viable alternative explanation. There was no energy barrier for cells to interact in a primary minimum for all roughness conditions because of the near neutral charge of the cell ($\zeta_{c}$ ranging from −2.1 to −5.9 mV as the IS increased from 1 to 100 mM) and negatively charged SWI ($\zeta_{sw}$ ranging from −63.8 to −29.8 mV).

Figure 5. Contour plots of $\epsilon_{1}$ (A), $\epsilon_{2}$ (B), and $\beta_{1}$ (C) for an oocyst and quartz sand for the CH+NR-Both condition when the IS = 10 mM NaCl. Parameter values were the same as in Figure 2 (Table 1), with the exception that $f_{sr} = f_{cr}$ was now varied between 0.01 and 1 (shown on a log scale) and $h_{sr} = h_{cr}$ ranged from 0 to 80 nm. Values $0 < \beta_{1} < 1$ were interpolated by the graphing program.

Figure 6. Contour plots of $\epsilon_{1}$ (A) and $\beta_{1}$ (B) for a 100 nm colloid and quartz sand for the CH+NR-Both condition when the IS = 10 mM NaCl. Other parameter values were the same as in Figure 2 (Table 1), with the exception that $f_{sr} = f_{cr}$ was now varied between 0.01 and 1 (shown on a log scale) and $h_{sr} = h_{cr}$ ranged from 0 to 80 nm. Values $0 < \beta_{1} < 1$ were interpolated by the graphing program.
Figure 7. Contour plots of $\beta_1$ for an oocyst and quartz sand for the NR-Both condition when the IS = 1 (A), 10 (B), and 100 (C) mM NaCl. Parameter values are given in Table 1. Values $0 < \beta_1 < 1$ were interpolated by the graphing program.
systematically study these fundamental issues for many commercial and industrial applications.

**CONCLUSIONS**

An approach was developed to determine the interaction energy between a colloid and the SWI or another colloid that accounts for binary NR and CH on both surfaces. In particular, the mean interaction energy was determined as a linear combination of interaction energies associated with the NR and CH fractions on both surfaces within the zone of electrostatic influence. Numerical experiments were subsequently conducted to investigate the roles of NR and CH parameters, colloid size, and solution IS on interaction energy parameters, the probability for colloid immobilization and release, and reversible and irreversible retention or aggregation. CH primarily influenced the interaction energy by reducing the energy barrier and increasing the depths of the primary and secondary minima when the SWI was smooth, especially for higher CH fractions, for smaller colloid sizes, and for colloid−colloid than colloid-SWI interactions. Roughness mainly produced primary minimum interactions, even under electrostatically unfavorable conditions, that were reversible or irreversible depending on the roughness fraction and height. The influence of NR was also coupled with the solution IS due to its influence on the zeta potentials and the double layer thickness. An increase in solution IS tended to produce an even shallower primary minimum. Consequently, changes in solution IS influenced the NR combinations that contributed to reversible and irreversible colloid retention and suspension stability. Only a fraction of the roughness combinations produced irreversible colloid retention in the absence of an energy barrier. Not all the surface area is therefore expected to contribute to colloid retention under electrostatically favorable conditions. In the presence of an energy barrier, an increase in IS produced more NR combinations for irreversible retention, and colloid retention was therefore expected to increase with IS. Conversely, in the absence of an energy barrier, an increase in IS produced a decrease in irreversible colloid retention when the primary minimum was shallow. These observations indicate that NR can provide a viable alternative explanation for anomalous colloid retention and stability behavior that has previously been attributed to electrosteric repulsion (e.g., a decrease in colloid retention with an increase in solution IS; reversible colloid retention under favorable conditions; and diminished colloid retention and enhanced colloid stability due to adsorbed surfactants, polymers, and/or humic materials that alter roughness properties). The developed approach can be used...
to design surfaces with specific NR and CH features to enhance or diminish colloid retention and/or stability. It can also be employed to investigate colloid retention and stability on natural surfaces that exhibit distributions of roughness parameters.

**ASSOCIATED CONTENT**

* Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.langmuir.7b02445.

Interaction energy calculations (S1); plot of $\epsilon_1$ as a function of $\Phi_{\text{max}}$ when $\Phi_{\text{2min}} = 0$ and $\Phi_{\text{1min}} = -\infty$ (unfavorable electrostatic conditions), and $\epsilon_{r1}$ as a function of $\Phi_{\text{1min}}$ when $\Phi_{\text{2min}} = 0$ and $\Phi_{\text{max}} = 0$ (favorable electrostatic conditions); plots of $\Phi_{\text{1min}}$ for a physically and chemically homogeneous oocyst and SWI when the IS = 10 mM and the zeta potential of the oocyst and the SWI was varied between $-60$ and $60$ mV (PDF)

**AUTHOR INFORMATION**

Corresponding Author

*Phone: 951-369-4857. E-mail: Scott.Bradford@ars.usda.gov.

**ORCID**

Scott A. Bradford: 0000-0002-3260-2968

**Notes**

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**REFERENCES**


**Figure 9.** Contour plots of $\beta_1$ for 100 (A), 1000 (B), and 5000 (C) nm sized colloids for the NR-Both condition when the IS = 100 mM NaCl. Colloid–colloid interactions are considered and parameter values are given in Table 1. In this case, $h_s = h_c$ and $f_s = f_c$ denotes that the roughness height and fraction, respectively, were the same on both colloids. Values $0 < \beta_1 < 1$ were interpolated by the graphing program.


SUPPORTING INFORMATION

Contributions of Nanoscale Roughness to
Anomalous Colloid Retention and Stability Behavior

Scott A. Bradford¹, Hyunjung Kim², Chongyang Shen³, Salini Sasidharan⁴, and Jianying Shang³

¹US Salinity Laboratory, USDA, ARS, Riverside, CA
²Department of Mineral Resources and Energy Engineering, Chonbuk National University, 664-14 Duckjin, Jeonju, Jeonbuk 561-756, Republic of Korea
³Department of Soil and Water Sciences, China Agricultural University, Beijing, China 100193
⁴Department of Environmental Sciences, University of California, Riverside, 92521

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The supporting information contains details pertaining to interactions energy calculations (S1). Figure S1 presents a plot of $\varepsilon_1$ as a function of $\Phi_{\text{max}}$ when $\Phi_{2\text{min}}=0$ and $\Phi_{1\text{min}}=-\infty$ (unfavorable electrostatic conditions), and $\varepsilon_{r1}$ as a function of $\Phi_{1\text{min}}$ when $\Phi_{2\text{min}}=0$ and $\Phi_{\text{max}}=0$ (favorable electrostatic conditions). Figure S2 presents plots of $\Phi_{1\text{min}}$ for a physically and chemically homogeneous oocyst and SWI when the IS=10 mM and the zeta potential of the oocyst and the SWI were varied between -60 to 60 mV. This information is available free of charge via the Internet at http://pubs.acs.org

**S1 – Interaction Energy Calculations**

The value of $\Phi_s$ between a colloid and the SWI, or another colloid, was considered to be the sum of electrostatic, van der Waals, and Born repulsion interaction energies:

$$\Phi_s(h) = \Phi_{s}^{\text{el}}(h) + \Phi_{s}^{\text{vdW}}(h) + \Phi_{s}^{\text{Born}}(h) \quad [S1]$$

where $\Phi_{s}^{\text{el}} [\text{ML}^2\text{T}^{-2}]$, $\Phi_{s}^{\text{vdW}} [\text{ML}^2\text{T}^{-2}]$, and $\Phi_{s}^{\text{Born}} [\text{ML}^2\text{T}^{-2}]$ are the electrostatic, van der Waals, and Born interaction energies on the smooth surface, respectively. The value of $\Phi_{s}^{\text{el}}$ was determined using the constant surface potential interaction expression of Hogg et al.$^1$ for a sphere-plate interaction as:

$$\Phi_{s}^{\text{el}}(h) = \pi \varepsilon \varepsilon_{0} r_c \left\{ 2 \zeta_1 \zeta_2 \ln \frac{1+\exp(-\kappa h)}{1-\exp(-\kappa h)} + (\zeta_1^2 + \zeta_2^2) \ln[1 - \exp(-2\kappa h)] \right\} \quad [S2]$$

where $\varepsilon$ (dimensionless) is the dielectric constant of the medium, $\varepsilon_{0} [\text{M}^{-1}\text{L}^{-3}\text{T}^4\text{A}^{-2}]$, $r_c [\text{L}]$ is the colloid radius, $\zeta_1$ is the zeta potential of the colloid, $\zeta_2$ is the zeta potential of the collector, and $\kappa [\text{L}^{-1}]$ is the Debye-Huckel...
parameter. The value of $\Phi^{vdW}$ for a sphere-plate interaction was determined using the expression by Gregory$^2$ as:

$$\Phi^{vdW}_s(h) = -\frac{A_{123}r_c}{6h} \left[1 + \frac{14h}{\lambda}\right]^{-1}$$  \[S3\]

where $A_{123}$ [ML$^2$T$^{-2}$] is the Hamaker constant, and $\lambda$ is a characteristic wavelength that was taken as 100 nm.$^2$ The value of $\Phi^{Born}$ was calculated from Ruckenstein and Prieve$^3$ for a sphere-plate interactions as:

$$\Phi^{Born}_s(h) = \frac{A_{123}\sigma_e^6}{7560} \left[\frac{8r_c h + 1}{(2r_c + 7)^2} + \frac{6r_c - h}{h^2}\right]$$  \[S4\]

The collision diameter, $\sigma_c$, was taken as 0.26 nm in order to achieve a primary minimum depth at 0.157 nm, a commonly accepted distance of closest approach.$^4$

Slightly modified versions of Eqs. [S2] and [S3] were employed for colloid-colloid interactions. In particular, the value of $r_c$ was replaced by $r_{c1}r_{c2}/(r_{c1}+r_{c2})$ for sphere-sphere interactions; where $r_{c1}$ [L] and $r_{c2}$ [L] are the radii of two colloids denoted with subscripts 1 and 2, respectively. Unfortunately, Eq. [S4] cannot be simply modified in a similar manner to determine the Born repulsion for sphere-sphere geometry. In this case, the expression of Oliveira$^5$ was employed to determine Born repulsion as:

$$\Phi^{Born}_s(h) = \frac{A_{123}H_{min}^6}{168h^7} \left[\frac{r_{c1}r_{c2}}{r_{c1}+r_{c2}}\right]$$  \[S5\]

where $H_{min}$ [L] is the value of closest approach equal to 0.157 nm.

All interaction energies were made dimensionless by dividing by the product of the Boltzmann constant ($k_B = 1.38 \times 10^{-23}$ J K$^{-1}$) and the absolute temperature ($T_K$).
Cited Literature


(S4) van Oss, C.J. *Interfacial Forces in Aqueous Media*. Marcel Dekker (New York), **1994**.

Figure S1. Plots of $\varepsilon_1$ as a function of $\Phi_{\max}$ when $\Phi_{2\min}=0$ and $\Phi_{1\min}=-\infty$ (unfavorable electrostatic conditions), and $\varepsilon_{r1}$ as a function of the magnitude of $\Phi_{1\min}$ when $\Phi_{2\min}=0$ and $\Phi_{\max}=0$ (favorable electrostatic conditions).
Figure S2. Plots of $\Phi_{1\text{min}}$ for a physically and chemically homogeneous oocyst and SWI when the IS=10 mM and the zeta potential of the oocyst and the SWI were varied between -60 to 60 mV.