Anomalous Attachment Behavior of Nanoparticles inside Narrow Channels

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Understanding nanoparticle (NP) attachment inside narrow passages such as the pore throats of porous media and plant and animal tissues is critically important to assess the potential ecological and toxicological impact of NPs. This study investigated the attachment of a NP inside a cylindrical nano-sized channel with finite wall thickness at various ionic strengths (ISs) by calculating the Derjaguin–Landau–Verwey–Overbeek (DLVO) interaction energy using a modified surface element integration technique. Results show that there is a critical value of the ratio of the inner channel diameter to NP diameter (RCN) at which the repulsive energy barrier reaches a maximum at a given IS and NP transport is most favored. A non-monotonic variation of the energy barrier with IS was observed for RCNs smaller than the critical value. The repulsive energy barrier disappears at all ISs when the NP diameter is close to the inner channel diameter, resulting in favorable attachment at primary minima. The attached NP cannot be detached in these cases by a disturbance of system conditions because of increased primary-minimum depths and accordingly enhanced adhesive forces. For a given RCN, decreasing the channel thickness can increase and decrease the interaction energy barrier and primary-minimum depth for a NP inside the channel, respectively. Accordingly, NP attachment in primary minima is inhibited whereas transport is favored in channels with thin walls. These theoretical results provide plausible explanations of experimental observations that the retention of colloids in pore throats of porous media via straining is chemically favorable (i.e., no repulsive energy barrier exists) even at very low ISs and irreversible to reduction of the solution IS, and that NPs are favorably attached in narrow passages such as plant tissues and membrane pores.

Abbreviations: DA, Derjaguin approximation DL, double layer; DLVO, Derjaguin–Landau–Verwey–Overbeek; IS, ionic strength; NFC, nanoparticle–flat plate configuration; NP, nanoparticle; PB, Poisson–Boltzmann; RCN, ratio of inner channel diameter to nanoparticle diameter; SEI, surface element integration; VDW, van der Waals.

Investigation of the attachment of nanoparticles (NPs) inside a nano-sized channel (as opposed to on a surface) is critical to understanding NP transport behavior in a variety of environmental processes and engineered applications. Examples include transport of nanomaterials in pore throats of porous media (Fang et al., 2013; May and Li, 2013; Wang et al., 2014; Knappenberger et al., 2015), translocations of NPs in plant tissues such as stems and leaves (Zhu et al., 2008; Corredor et al., 2009; Lin et al., 2009; Wu et al., 2012; Giraldo et al., 2014), transport of NPs in blood vessels during drug delivery (Blanco et al., 2015), filling of carbon nanotubes with metal NPs for applications in catalysis, polymers, and electronics (Regan et al., 2004; Tessonnier et al., 2009; La Torre et al., 2010), and trapping and handling of single NPs in solution using nanochannels for potential applications in chemistry, biotechnology, and clinical medicine (Sharma et al., 2017).

Attachment of a NP on a collector surface is governed by colloidal interaction energies that act between them (Elimelech and O’Melia, 1990; Elimelech et al., 2013). These colloidal interactions include van der Waals (VDW) attraction, electrical double layer (DL) force, and short-range repulsion (e.g., hydration and steric repulsion), which are quantitatively described by the well-known extended Derjaguin–Landau–Verwey–Overbeek (DLVO) theory (Verwey and Overbeek, 1948; Ryan and Elimelech, 1996; Israelachvili,
Exact evaluation of the aforementioned types of interaction energy requires complex and tedious numerical calculations even for simple interaction configurations (e.g., a spherical particle interacting with a flat plate). Alternatively, the Derjaguin approximation (DA) has been frequently used to derive analytical expressions for approximate estimation of the DLVO energy by scaling two interacting curved surfaces into pairs of parallel plates (Hogg et al., 1966; Lin and Wiesner, 2010). The applicability of the DA technique, however, is limited to large particles. Bhattacharjee and Elimelech (1997) and Bhattacharjee et al. (1998a) developed the surface element integration (SEI) approach, which has overcome the limitations of the DA technique and can thus accurately determine the interaction energy even for NPs.

The DA and SEI techniques have been frequently used to calculate the interaction energy between a NP and an open collector surface (e.g., a planar surface). The calculations reveal that only primary minima are present and available for NP attachment under favorable conditions (i.e., in the absence of a repulsive energy barrier). In addition to the primary minimum attachment, NPs can also attach at secondary minima under unfavorable chemical conditions if the secondary energy wells are deep enough to prevent the NPs from being detached by applied forces such as hydrodynamic shear and Brownian diffusion (Hahn and O’Melia, 2004; Hahn et al., 2004; Redman et al., 2004; Liu et al., 2009; Landkamer et al., 2013). Increasing solution ionic strength (IS) decreases the interaction energy barrier and increases the secondary minimum depth under unfavorable conditions and accordingly increases attachment in both primary and secondary minima (Hahn et al., 2004; Shen et al., 2011).

The interaction energy for a NP inside a closed surface has received very limited attention. Specifically, Bhattacharjee and Sharma (1995, 1996) used the SEI technique to estimate VDW interaction energies for spherical NPs in a cylindrical pore at every location. Bhattacharjee and Sharma (1996, 1997) further used the SEI technique to estimate the total interaction energy for this interaction geometry by including VDW and DL energies and short-range repulsions (i.e., hydration or acid–base interaction). These studies, however, considered only interaction of the NP with the approaching half pore surface, causing a certain amount of interaction energy even at the cylindrical pore axis. The interaction energy at these locations will be zero if the effects of both the approaching and more distant pore surfaces are considered. This is because the interaction energies from the approaching and more distant pore surfaces cancel each other out at the pore axis due to symmetry of the interaction geometry. In addition, the aforementioned studies assumed that the thicknesses of channels and pore walls were infinitely large. Although Zhdanov (2017) addressed the interaction configuration of spherical NPs inside a cylindrical channel with finite thickness, they only calculated the VDW interaction energy at the channel axis by developing analytical expressions using the Hamaker approach. The total interaction energy for a NP inside a channel of finite thickness at any location has not been evaluated. To date, understanding of the mechanisms controlling the attachment of NPs in a closed surface has not been completed. For example, whether the trend for the variation of interaction energy parameters (e.g., maximum energy barrier and secondary minimum depth) with IS for such interaction geometry is similar to that of the interaction of a NP with an open collector surface as shown above is still unclear.

This study systematically examined the interaction energy for a spherical NP inside a cylindrical nano-sized channel (cf., Fig. 1) on the interaction energy. We showed that the thickness of the channel and the ratio of the inner diameter of the channel to the NP diameter (RCN) play a critical role in controlling the variation of the interaction energy with the separation distance between the NP and the inner channel surface and, consequently, the NP attachment onto the surface. The interaction between the NP and the interior surface of the channel is significantly different from that between the NP and an open collector surface at small RCN values due to the significant influence of the other half channel surface. The findings in this study can explain various experimental observations in the literature and have important implications for industrial and environmental applications that involve NP transport through a variety of biological materials (e.g., plant and human tissues) and the use of nanochannels for NP delivery.

**Theory**

The SEI technique (Bhattacharjee and Elimelech, 1997; Bhattacharjee et al., 1998a, 1998b) was modified to calculate the interaction energy for a spherical NP inside a cylindrical nanochannel in Fig. 1. The Cartesian coordinate system was adopted for the interaction configuration, with the z axis superposing the center line of the channel and the y axis passing through the NP.

![Fig. 1. Coordinate system used to describe a spherical nanoparticle (NP) interacting with the interior surface of a cylindrical nanochannel](image)
The ring PAQA is the cross-section of the channel cut by the xy plane. The xz plane divides the channel into two half channels PAQ and PAQ', and the yz plane divides the channel into two half channels A'PA and A'QA. The total force that acts on the NP in the channel is due to the difference in the forces from the half channels PAQ and PAQ', and its direction is along the y axis (or line O-T, where O and T are the centers of the ring PAQA and the NP, respectively) due to symmetry of the interaction configuration. Note that no net force component exists along the z axis because the forces from the half channels A'PA and A'QA cancel each other out. There is also no force component along the x axis when the channel is open-ended.

The NP surface was discretized into small area elements. Each surface element dS interacts with the corresponding element dA in, and dA out on the inner and outer surfaces, respectively, of the half channel PAQ (Wu et al., 2013). The element dS also interacts with the corresponding elements dA in' and dA out' on the inner and outer surfaces, respectively, of the half channel PAQ'. The projected areas of the elements dA in, dA out, dA in', and dA out' on the xz plane are the same as that of the element dS on the plane (denoted as dS'). The differential interaction energies dU S,dfin, dU S,dfout, dU S,din, or dU S,dout for the element dS with dA in, dA out, dA in' or dA out' are calculated as

$$dU_{S,din} = (\mathbf{n}, \mathbf{k}) \left( \mathbf{n}_A \cdot \mathbf{k}_A \right) E_{DL}(h_{SA}) dS$$

$$dU_{S,dout} = (\mathbf{n}, \mathbf{k}) \left( \mathbf{n}_A \cdot \mathbf{k}_A \right) E_{DL}(h_{SA}) dS$$

$$dU_{S,din} = (\mathbf{n}, \mathbf{k}) \left( \mathbf{n}_A \cdot \mathbf{k}_A \right) E_{DL}(h_{SA}) dS$$

$$dU_{S,dout} = (\mathbf{n}, \mathbf{k}) \left( \mathbf{n}_A \cdot \mathbf{k}_A \right) E_{DL}(h_{SA}) dS$$

where \( \mathbf{k}, \mathbf{k}_A, \mathbf{k}_A', \mathbf{k}_A'' \) and \( \mathbf{k}_A'' \) are the outward unit vectors normal to the NP surface, inner surface of half channel PAQ, outer surface of half channel PAQ, inner surface of half channel PAQ', and outer surface of half channel PAQ', respectively; \( \mathbf{n}, \mathbf{n}_A, \mathbf{n}_A' \) and \( \mathbf{n}_A'' \) are the unit vectors directed toward the positive y axis; \( h_{SA}, h_{SA}', h_{SA}'', h_{SA}'' \) are the distance between the elements dS and dA in, dA out, dA in', or dA out', and \( E(h) \) is interaction energy per unit area between two infinite planar surfaces.

The total interaction energy \( U_{DL} \) between the NP and the channel was calculated as the sum of VDW attraction \( (U_{VDW}) \), DL interaction energy \( (U_{DL}) \), and short-range repulsion. The short-range repulsion was determined by calculating the Born potential energy \( U_{BR} \) (Ruckenstein and Prieve, 1976). The DL interaction is a surface force, so only interaction between the NP and the inner surface of the channel needs to be considered for calculating \( U_{DL} \). The value of \( U_{DL} \) can be obtained by summation of the differential interaction energy \( dU_{DL} \) for each dS on the entire NP surface with the corresponding elements on the inner surface of the channel. Using Eq. [1] and [3], the expression used to calculate \( U_{DL} \) is

$$U_{DL} = \sum_s \left( dU_{S,din} - dU_{S,dout} \right)$$

$$= \sum_s \left( (\mathbf{n}, \mathbf{k}) \left( \mathbf{n}_A \cdot \mathbf{k}_A \right) E_{DL}(h_{SA}) dS \right)$$

$$- (\mathbf{n}, \mathbf{k}) \left( \mathbf{n}_A \cdot \mathbf{k}_A' \right) E_{DL}(h_{SA'}) dS$$

Similarly, the equation used to calculate \( U_{BR} \) is written as

$$U_{BR} = \sum_s \left( dU_{S,din} - dU_{S,dout} \right)$$

$$= \sum_s \left( (\mathbf{n}, \mathbf{k}) \left( \mathbf{n}_A \cdot \mathbf{k}_A \right) E_{BR}(h_{SA}) dS \right)$$

$$- (\mathbf{n}, \mathbf{k}) \left( \mathbf{n}_A \cdot \mathbf{k}_A' \right) E_{BR}(h_{SA'}) dS$$

The VDW interaction is a volume force, so the influence of both interior and outer surfaces of the channel has to be considered for calculating \( U_{VDW} \) in the SEI technique. Using Eqs. [1–4], the expression used to calculate \( U_{VDW} \) is given by

$$U_{VDW} = \sum_s \left( dU_{V,din} - dU_{V,dout} \right)$$

$$= \sum_s \left( (\mathbf{n}, \mathbf{k}) \left( \mathbf{n}_A \cdot \mathbf{k}_A \right) E_{VDW}(h_{SA}) dS \right)$$

$$- (\mathbf{n}, \mathbf{k}) \left( \mathbf{n}_A \cdot \mathbf{k}_A' \right) E_{VDW}(h_{SA'}) dS$$

The expressions used to calculate \( E_{VDW}(b) \) and \( E_{BR}(b) \) are (Hamaker, 1937; Oliveira, 1997)

$$E_{VDW}(b) = -\frac{A_H}{12 \pi b^3}$$

$$E_{BR}(b) = \frac{A_H H_0^6}{48 \pi b^8}$$

where \( A_H \) is the Hamaker constant and \( H_0 \) is the minimum separation distance between the NP and the channel, taken as 0.158 nm (Hoek and Agarwal, 2006). The value of \( E_{DL}(b) \) was determined by exactly solving the one-dimensional nonlinear Poisson–Boltzmann (PB) equation using the method of Devereux and de Bruyn (1963). This method can accurately determine \( E_{DL}(b) \) without using any assumption. Details for determination of the \( E_{DL}(b) \) are given in the Supplemental Material.

When the NP is outside the open-ended channel, the influence of both the interior and outer surfaces of the channel has to be considered for calculating \( U_{VDW} \) and \( U_{DL} \). The expressions used to calculate \( U_{VDW} \) and \( U_{DL} \) are written as
The equation used to calculate $U_{BR}$ for the NP outside the channel is

$$U_{BR} = \sum_S \left( dU_{S,4n}^{DL} + dU_{S,4n}^{DL} - dU_{S,4n}^{DL} - dU_{S,4n}^{DL} \right)$$

$$= \sum_S \left[ \left(n, k, A_{4n} \right) E_{DL}^{4n} \left(h_{S,4n} \right) dS \right]$$

Note that when the inner channel diameter is infinitely large, the interaction configuration for the NP inside or outside the channel will become the NP–flat plate interaction configuration (NFC). MATLAB programs were developed to implement the calculations of the energies for these interaction configurations in three-dimensional space.

**Results and Discussion**

Unless otherwise specified, the spherical NPs and nano-channels were assumed to be silica NPs and carbon nanotubes, respectively. The interaction energies were calculated for the silica NPs inside a nanotube in NaCl solutions at ISs of 1, 10, 100, and 200 mM. Zeta potentials of the silica NPs and carbon nanotubes across the IS range are shown in Supplemental Table S1. A value of $9.81 \times 10^{-20}$ J was chosen as the Hamaker constant for the silica–water–carbon system (Wu et al., 2013).

Figure 2 presents the interaction energy maps for a 70-nm silica NP inside a channel of 80-nm inner diameter and 5-nm wall thickness at 1 and 10 mM. The scale bar to the right of each plot represents the interaction energy in units of $kT$ ($k$ is the Boltzmann constant and $T$ is the absolute temperature). A positive or negative value of interaction energy represents that the NP experiences repulsion or attraction, respectively (i.e., pointing radially to or from the center of the cross-section of the channel).

Figure 2. Derjaguin–Landau–Verwey–Overbeck (DLVO) interaction energy maps for a 70-nm silica nanoparticle (NP) at a cross-section of a nanochannel with 80-nm inner diameter and 5-nm thickness at ionic strengths of 1 and 10 mM. The scale bar to the right of each plot represents the interaction energy in units of $kT$ ($k$ is the Boltzmann constant and $T$ is the absolute temperature). A positive or negative value of interaction energy represents that the NP experiences repulsion or attraction, respectively (i.e., pointing radially to or from the center of the cross-section of the nanochannel).
considered the NP interaction with only the approaching inner half channel surface. Interestingly, Fig. 2 shows that the repulsive energy barrier is greater at 10 mM than that at 1 mM, in contrast to the decrease in the repulsive energy barrier with increasing IS for a colloid interacting with an open collector surface (Hahn and O’Melia, 2004; Hahn et al., 2004). Because the interaction energies are equal at the same distance from the CCS, only the interaction energy along a radial direction of the cross-section (e.g., negative $y$ direction in Fig. 1) is considered below.

Figure 3 compares the interaction energy profiles between the 70-nm silica NP and a flat plate with those for the NP inside a channel of different inner diameters (74 and 200 nm) along a radial direction at different solution ISs. The thicknesses of the channels and the flat plate are 5 nm. As expected, the energy barrier for the NFC decreases monotonically with increasing IS. Hence, the silica NP is more readily attached in primary minima at higher IS. Particularly, the energy barrier completely disappears at 200 mM, and this chemical condition becomes favorable for NP attachment. For the NP inside the 200-nm channel, the variation of the energy barrier with IS is similar to that of the NFC. However, the primary minimum depth ($U_{pri}$) for the NP inside the channel is larger than that of the NFC at a given IS, which can be explained by the concept of “interaction volume” developed by Huang et al. (2010). The interaction volume is defined as the volume between the leading half of a spherical particle and a substrate surface. Evidently, the interaction volume is smaller for a NP interacting with the approaching half channel surface (e.g., half channel PAQ in Fig. 1) than that of the NFC. Huang et al. (2010) demonstrated that smaller interaction volumes between a particle and a substrate surface result in larger interaction energies because the mean plane of the substrate surface is closer to the apex of the probe particle. Therefore, the value of $U_{pri}$ is larger for the NP inside the 200-nm channel. Because the adhesive force that acts on a particle is proportional to the $U_{pri}$ (Israelachvili, 2010), the silica NP can be attached more strongly in the primary minimum inside the 200-nm channel than in the NFC case.

Interestingly, a non-monotonic variation of the energy barrier with IS is present when the inner diameter of the channel is decreased to 74 nm (cf., Fig. 3). In this case, the absence of an energy barrier occurs at both 200 and 1 mM. The absence of an energy barrier at 1 mM occurs because the repulsive energy barrier between the silica NP and the approaching half channel (e.g., PAQ in Fig. 1) is eliminated by the strong repulsion from the other half channel (PA’Q). Therefore, the silica NP can attach in the primary minima in the channel even at this low IS, which is considered very unfavorable for particle attachment on open collector surfaces. For the same reason, the maximum energy barriers at 10 and 100 mM (2.6 and 3.9 $kT$, respectively) are significantly smaller than those calculated for the NP inside the 200-nm channel or for the NFC. These maximum energy barriers are comparable to the average kinetic energy of a colloid (1.5 $kT$); thus the NP could overcome the energy barriers by Brownian diffusion and attach in the primary minima. Additionally, the primary-minimum depth (and

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**Fig. 3.** Derjaguin–Landau–Verwey–Overbeek (DLVO) interaction energy profiles for a 70-nm silica nanoparticle (NP) interacting with (a) a flat plate or inside a channel of (b) 200-nm or (c) 74-nm inner diameter along a radial direction at different ionic strengths. The thicknesses of the channels and the flat plate are 5 nm, $H$ is the separation distance, $R$ is the inner radius of the tube, $r$ is radius of the NP, and $U_T$ is the total interaction energy in units of $kT$ ($k$ is the Boltzmann constant and $T$ is the absolute temperature).
correspondingly the adhesive force) is further increased for the NP inside the 74-nm channel due to a smaller interaction volume.

Figure 4 presents calculated values of $U_{\text{pri}}$, the maximum energy barrier ($U_{\text{max}}$), and the secondary-minimum depth ($U_{\text{sec}}$) for a 70-nm silica NP interacting with channels of different inner diameters at different ISs. The value of $U_{\text{pri}}$ increases with decreasing inner diameter of the channel because the interaction volume is smaller for the smaller RCN. For a given IS, there is a critical RCN value where $U_{\text{max}}$ reaches the maximum. Below this critical value, $U_{\text{max}}$ decreases with decreasing channel inner diameter. This is because $U_{\text{max}}$ also increases with decreasing interaction volume. However, when the RCN is very small, the repulsive energy barrier between the NP and the approaching half channel will be reduced due to repulsion from the other half channel in the opposite direction. When the inner diameter of the channel is significantly larger than the NP diameter, the value of $U_{\text{max}}$ will approach that of the NFC. This is geometrically logical because the colloid–channel interaction configuration becomes NFC when the inner diameter of the channel is infinitely large. Similarly, there is also a critical value for the RCN at which $U_{\text{sec}}$ reaches the maximum. However, all the values of $U_{\text{sec}}$ are smaller than the average kinetic energy of a colloid. Hence, these shallow secondary energy wells in the channels cannot cause immobilization of the 70-nm NP due to Brownian diffusion.

The variations of $U_{\text{pri}}$, $U_{\text{max}}$, and $U_{\text{sec}}$ with RCN shown in Fig. 4 were obtained by fixing the NP diameter and changing the inner diameter of the channel. Similar results were obtained by fixing the inner diameter of the channel and changing the NP diameter (see Supplemental Fig. S1). These results reveal that the critical RCN value, where $U_{\text{max}}$ reaches the maximum, is optimal for delivering NPs using nanochannels because this condition is most unfavorable for NP attachment. The unfavorable condition can be further enhanced when the thickness of the channel ($L$) is very small (e.g., $L \leq 5$ nm in Supplemental Fig. S2) because $U_{\text{max}}$ increases and $U_{\text{pri}}$ decreases with decreasing channel thickness due to reduction of the VDW attractive energy. It is worthwhile mentioning that when the NP diameter approaches the inner diameter of the channel, the interaction energy barrier can disappear at all solution ISs considered (e.g., Fig. 3c). This provides a plausible explanation for the observations that NPs are readily attached inside channels at narrow locations (La Torre et al., 2010; Mahadevan et al., 2013; Peng and Li, 2017). This theoretical result also explains why colloids are favored to be retained in narrow pore throats of a porous medium via straining even at very low ISs and such retention is irreversible to IS reduction (Bradford et al., 2002; Auset and Keller, 2006; Li et al., 2006a; Kuznar and Elimelech, 2007). Note that if the NPs are positively charged (e.g., iron oxide NPs), the shape of the DLVO interaction energy profiles for the NPs inside the negatively charged channel is similar to that of the NFC, namely, only primary minima are present in the energy profiles (cf., Supplemental Fig. S3). Furthermore, the value of $U_{\text{pri}}$ increases with decreasing RCN due to reduced interaction volume (Supplemental Fig. S4).

![Figure 4](image)

**Fig. 4.** Calculated (a) primary-minimum depths ($U_{\text{pri}}$), (b) maximum energy barriers ($U_{\text{max}}$), and (c) secondary-minimum depths ($U_{\text{sec}}$) in units of $kT$ ($k$ is the Boltzmann constant and $T$ is the absolute temperature) for a 70-nm silica nanoparticle interacting with channels of different inner diameters at different ionic strengths. The thickness of the tube is 5 nm.

For a silica NPs outside of the nanochannel, the energy barrier increases monotonically with decreasing IS (Supplemental Fig. S5), which is similar to the case of the NFC. At a given IS,
$U_{\text{max}}$ decreases with decreasing RCN due to increased interaction volume (Fig. 5), and $U_{\text{max}}$ is further decreased when the thickness of the channel is very small (Supplemental Fig. S6). Hence, it is easier for the silica NP to attach in primary minima on the outer surface of a channel with smaller diameter and thickness. On the other hand, the attached NP can be readily detached by perturbations in system conditions (e.g., by increasing hydrodynamic shear) because the values of $U_{\text{pri}}$ and accordingly the adhesive force are also reduced. Figure 5 and Supplemental Fig. S6 additionally show that $U_{\text{sec}}$ decreases and increases with RCN and channel thickness, respectively. However, all the values of $U_{\text{sec}}$ are smaller than the average kinetic energy of a colloid; therefore, the silica NP cannot be immobilized on the outer channel surfaces via secondary-minimum association.

When multiple NPs are present inside a channel, the NPs may aggregate and the aggregate can facilitate attachment on the inner channel surface when its size approaches the inner channel diameter. Such attachment due to enlarged NP size may also occur for those NPs that can redissolve in solutions and undergo Ostwald ripening (La Torre et al., 2010; Thanh et al., 2014). Note that the DL interaction energies were calculated exactly using the constant surface potential condition to solve the nonlinear PB equation analytically (Devereux and de Bruyn, 1963). If constant surface charge or a linear superposition approximation condition is used to estimate the DL energies, the energy barrier and primary-minimum depth will be increased and decreased, respectively (Gregory, 1975; Swanton, 1995; Adamczyk and Weronski, 1999). Accordingly, attachment would be inhibited and the NPs would be more mobile inside the nanochannels. However, the trends in variation of $U_{\text{pri}}$, $U_{\text{max}}$, and $U_{\text{sec}}$ with IS, RCN, and $L$ do not change even if a constant surface charge or linear superposition approximation condition is used (see Supplemental Fig. S7).

Although the zeta potentials of cylindrical channels were taken as those of carbon nanotubes in our work, the general trends of variation of the interaction energy parameters with IS, RCN, and $L$ also do not change when zeta potentials of other materials (e.g., quartz sand) are adopted. Moreover, the results remain the same when the short-range repulsion is considered as hydration instead of Born repulsion (cf., Supplemental Fig. S8). We only considered the channels with inner diameters above 70 nm so that fluid flow and electrostatic potential in the channels can still be described by Navier–Stokes and PB equations, respectively (Patrick and Nguyen, 2009; Hulings et al., 2015). In addition, we assumed that the surfaces of the channels are smooth and chemically homogeneous. The SEI technique can also be used to calculate the interaction energies for NPs inside channels in the presence of surface roughness and/or surface charge heterogeneity (Bhattacharjee and Elimelech, 1997; Bhattacharjee et al., 1998a, 1998b). The influence of surface physical and chemical heterogeneities on interaction energies for NPs inside nanochannels is an ongoing topic but beyond the scope of this study.

Cylindrical channels have been frequently used to represent pore geometries of porous media such as soil (Jury and Horton, 2004). Real soil pore morphologies, however, are very complex (Tuller and Or, 2001; Xiong et al., 2016). Our results, which are based on NP–cylindrical channel interactions, are applicable for explaining the attachment and detachment of NPs in symmetrical

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**Fig. 5.** Calculated (a) primary-minimum depths ($U_{\text{pri}}$), (b) maximum energy barriers ($U_{\text{max}}$), and (c) secondary-minimum depths ($U_{\text{sec}}$) in units of $kT$ ($k$ is the Boltzmann constant and $T$ is the absolute temperature) for a 70-nm silica nanoparticle outside channels of different inner diameters at different ionic strengths. The channel thickness is 10 nm.
pore throats even if they are not cylindrical. For example, irreversible attachment in primary minima can occur in pore throats that are confined between two collectors (i.e., the attachment at grain-to-grain contacts) (Li et al., 2006b; Shen et al., 2008) even at very low ISs because the interaction energy barriers from the two collector surfaces can cancel each other out. For a NP in an angular pore throat where multiple collector surfaces intersect, the NP is readily attached at primary minima in the area close to the vertex of the two intersecting surfaces where the repulsive energy barrier is reduced or even disappears (Li et al., 2017; Shen et al., 2017). This is because the energy barrier between the NP and one surface can be reduced by the interaction energy barrier from the other intersecting collector surface.

While our work considered only the interaction energies for a NP inside a channel, the obtained results are also applicable for explaining attachment of larger micro-particles inside channels. For example, a micro-particle can also attach in a microscale pore throat at primary minima at very low ISs if the pore size is close to the particle size. It is worthwhile mentioning that the nanoscale pore throats are commonly saturated with water under the prevalent water potential conditions in subsurface environments such as soil. In contrast, the degree of saturation of the microscale pore throats (i.e., capillary pores) frequently varies. Under unsaturated conditions, the micro-particle and pore surface are only partially immersed in solution. The interaction energy exists only between the surfaces immersed in the solutions. There is no repulsive interaction energy in the opposite direction due to the existence of air between the pore surface and the micro-particle. Therefore, the interaction of micro-particles with pore throats is more similar to the NFC case at low saturation.

Conclusions

Through systematic evaluation of the interaction energies of a negatively charged NP inside a negatively charged cylindrical nanochannel of finite thickness, we identified a critical RCN value at which the repulsive energy barrier reaches the maximum at a given IS. Hence, this condition is the most favorable for NPs to transport through narrow channels or for NP delivery using nanochannels. In the case of NP delivery using nanochannels, such facilitated transport can be further enhanced by reducing the channel thickness, which increases the energy barrier and decreases the primary-minimum depth and, consequently, the adhesive force. For small values of the RCN (i.e., the NP diameter is close to the inner diameter of the channel), the repulsive energy barrier can disappear completely even at very low ISs, resulting in favorable NP attachment in primary minima that is irreversible by disturbances to the system (e.g., a change in hydrodynamics). These theoretical results provide plausible explanations for the experimental observations that straining, i.e., retention of colloids in porous throats of porous media, is chemically favorable even at very low ISs and irreversible to reduction of the solution IS, and that NPs are preferentially attached in narrow passages of plant tissues and membrane pores.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (41671222, 41271009, 41501232), Beijing Nova Program (Z161100004916116), and National Key Research and Development Program of China (2017YFD0800301).

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