Translocation of nanoparticles through a polymer brush-modified nanochannel

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A basic understanding of the transport mechanisms of nanostructures in a polymer brush-modified nanochannel as well as the brush-nanostructure interactions at molecular level is important to design and fabricate emerging smart nano/microfluidic channels. In this work, we report coarse-grained molecular dynamics simulations of the translocation of nanoparticles through a cylindrical nanochannel coated with the polymer brush. The effects of the interparticle interaction and grafting density on the distribution and electrokinetic transport of nanoparticles are addressed in detail. Analysis of the distribution and velocity profiles of nanoparticles from the simulations indicate that the location of nanoparticles along the radial direction and their migration velocity are very sensitive to the change of interparticle interaction. We find complicated transport dynamics of nanoparticles under the influence of various grafting densities. The nanoparticles show markedly different translocation behavior upon increasing the grafting density, which depends on the counterion distribution, free room within the brush, nanoparticle-polymer friction, and brush configuration. Our results may serve as a useful starting point for the transport of nanostructures in polymer-modified channels and help to guide the design of novel smart nanofluidic channels for controlling the migration behavior of nanostructures. © 2012 American Institute of Physics.

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I. INTRODUCTION

Polymer brushes are a class of ultrathin polymer coatings consisting of polymer chains that are tethered with one end to a solid substrate with planar or curved surface.^{1,2} They can respond to many external stimuli such as salt ions, molecules, temperature, *pH*, electric potential, and light.³ Based on these responsive mechanisms, they can be used as “smart surfaces” to control the physicochemical properties of channel surfaces further implementing smart regulation of fluid transport. In various technologies of surface modifications, the polymer brushes represent an extensively adopted and effective surface modification approach. In the past few years, a rich variety of novel artificial nanochannels have been constructed, which is attracting widespread interest because their potential applications in biosensors, drug delivery, nanofluidic devices, etc.^{4,5} Experimentally, the integration of stimuli responsive polyelectrolyte brushes into solid-state single nanochannels can create tailor-made nanovalves resembling the functions of sophisticated biological ion channels.⁶ The gating mechanism is implemented by collapse-stretching conformational transition of the brushes responsive to *pH*. Coating amphoteric molecules (lysine or histidine) onto the inner surface of an asymmetric nanometer-scaled channel permits a broad set of rectification properties and enables a higher degree of ion transport regulation.⁷ In addition, it was also found that the functionality of biological ion channels can be enhanced significantly using plasma

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asymmetric chemical modification with various complicated functional molecules coated onto the wall of single nanochannels.⁸ With the development and application of nanofluidics, the nanochannels become key building blocks for the construction of lab-on-a-chip devices which provide useful research tools for ion transport, bionanotechnology, investigation of single-molecular behavior and biochemical analysis. Improving smart regulation of the nanochannels has become one challenging topic for lab-on-a-chip developments.

Understanding transport mechanisms of ions and molecules in nanochannels at the atomistic level is important to the design of nanofluidic channels. However, it is difficult to obtain atomistic details of ionic transport in the nanochannels through experimental observation. Molecular dynamics (MD) simulations can provide valuable insight into ionic and molecular transport through the nanochannels.^{9–14} A significant amount of simulation works have been performed to reveal fundamental aspects of electrokinetic transport. However, until now the theoretical investigations on the modulation of polymer brushes on ionic fluids are still insufficient. Recently, our group¹⁴ and other researchers^{13,15,16} have studied electroosmotic flow (EOF) in polymer-grafted nanochannels through MD simulations to elucidate effects of the polymer coatings on electroosmotic transport. Slater and co-workers have used coarse-grained MD simulations to predict the EOF in a cylindrical nanopore with neutral polymer coatings.^{13,16} Their results were found to be in agreement with experimental observations.¹⁷ Qiao has studied the EOF confined between two opposing walls grafted with polymer layers using full atomistic MD,¹⁵ which gave a good understanding of the mechanisms of electroosmotic transport modulated by neutral polymers. We have detailed the controlling mechanisms of the EOF through the polymer brush-modified channels in the environments with solvents of variable quality.¹⁴ Our results indicated that varying the solvent quality has a significant influence on the flow velocity, counterion distribution, and conformational behavior of the polymer brush. More recently, our group has investigated the valve mechanism for a polyelectrolyte-grafted channel under normal external electric fields,^{18,19} in which some new electrokinetic transport phenomena have been revealed.

These works mentioned above mainly focus on the transport of small ions and molecules through the polymer brush-modified channels under external fields. Wang *et al.* have studied the conformational transition of a free neutral chain confined in a cylindrical nanopore modified with a polymer brush using Monte Carlo method.²⁰ Their work identified a delicate interplay between a possible interpenetration of the free chain with the brush chains and the axial stretching of the free chains in the case of good solvent. There are few works dealing with the translocation of macromolecules and nanostructures in the nanochannels coated with the polymer brushes to address their transport dynamics at molecular level. On the contrary, a great deal of works has been dedicated to the electrophoresis of macromolecules (such as DNA and other polyelectrolyte chains) in bare micro/nanochannels.^{21–26} Recently, we have also reported the electrophoresis behavior of bottle-brush polyelectrolytes in an attractive nanochannel.²⁷ In the present work, our purpose is to study the translocation of charged nanoparticles under external electric fields. We will analyze the effects of the grafting density and brush-nanoparticle interaction on the distribution and movement characteristics of nanoparticles. The remainder of the paper is organized as follows: In Sec. II, we introduce our system model and the method details. Following that, the transport dynamics of nanoparticles and conformational behavior of polymer brushes are presented and discussed. We, finally, give a brief summary for this work.

II. MODEL AND SIMULATION METHOD

MD simulations are used to investigate the transport of nanoparticles through a polymer-grafted nanochannel under added electric fields. Grafted chains are modeled using a widely utilized, coarse-grained bead spring model.^{28,29} We take σ , m , and ϵ_{LJ} as length, mass, and energy units, respectively. All other units are derived from these basic units, such as time unit $\tau = (m\sigma^2/\epsilon_{LJ})^{1/2}$, velocity unit $u^* = (\epsilon_{LJ}/m)^{1/2}$, electric field $E^* = \epsilon_{LJ}\sigma^{-1}/(4\pi\epsilon_0\sigma\epsilon_{LJ})^{1/2}$ (ϵ_0 is the vacuum permittivity) and temperature unit $T^* = \epsilon_{LJ}/k_B$ (k_B is Boltzmann constant). Grafted end of each polymer chain with $N = 12$ monomers is fixed and selected randomly from wall particles of the nanochannel. To ensure an approximately uniform distribution, the smallest

separation between adjacent grafting points is larger than d_g which is slightly lower than the average separation $d = \rho_g^{-1/2}$. The grafting density ρ_g denotes the average number of polymer chains per unit area. The same arrangement of grafting points is used for each fixed grafting density. The wall of the channel is represented by stationary particles placed on a cylindrical surface. The radius and length of the nanochannel are set to 10.03σ and 95σ , respectively. The surface of each nanoparticle consists of 10 charged particles and 68 neutral ones which distribute evenly on its surface. The charged particles are randomly chosen from the surface particles. The radius of nanoparticles is fixed at $r_n = 2.49\sigma$. All simulations are performed at the same fluid density $\rho_f = 0.8\sigma^{-3}$ (including counterions, solvent particles, and monomers) and wall density of the channel $\rho_w = 1.0\sigma^{-3}$. Periodic boundary condition is applied along the channel direction, and the external electric field E is also exerted on charged particles (counterions and surface charged particles) along the channel direction. In this work, we set the electric field strength to $E = 0.2E^*$.

The short-range repulsive interaction is modeled by the Lennard-Jones (LJ) potential with a cutoff distance $r_c = 2^{1/6}\sigma$. To model the short-range attractive interaction, we introduce a larger cutoff distance $r_c = 2.5\sigma$.³⁰ In our simulations, four systems with different short-range interparticle interactions will be discussed: (I) For the good solvent case (MS), the cutoff radius of $r_c = 2.5\sigma$ is assigned to solvent-monomer pairs, while the purely repulsive LJ potential ($r_c = 2^{1/6}\sigma$) is used with respect to other particle pairs. (II) For the poor solvent case (MM), the cutoff radius for monomer-monomer pairs is set to $r_c = 2.5\sigma$, while other pair interactions are purely repulsive. (III) For the athermal solvent case (RP), all pair interactions are purely repulsive. (IV) We also study the case (MP) which the attractive interaction is only applied to monomer-nanoparticle pairs. Simulation snapshots for the systems are shown in Figure 1 as an aid for describing our model.

The chain's connectivity is maintained by a finitely extendable nonlinear elastic (FENE) potential with the spring constant $k_s = 30\epsilon_{LJ}/\sigma^2$ and the maximum bond length $R_0 = 1.5\sigma$.²⁸

FIG. 1. Simulation snapshots from our MD simulations at $\rho_g\sigma^2 = 0.1$. (a)–(d) corresponds to the system MM, MP, MS, and RP, respectively. Side cross-section views (left) and top views (middle and right) are provided for better visualization. Only the grafted chains and the wall of the channel are shown in the middle top views. The right top views only contain the nanoparticles and the wall. The arrow in (a) denotes the direction of external electric field. Color scheme: wall particles (gray), end grafting points (red), polymer brush (green), neutral (orange), and charged (blue) particles on nanoparticle surface, counterions (purple), and solvent particles (white).

Long-range electrostatic interaction between any two charged particles is calculated only in a cutoff distance r_{lc} . It is generally incorrect for three-dimensional cases to truncate the electrostatic interaction, but the present system only extends along one direction. We truncate the long-range interaction beyond a sufficiently large separation. The same idea is also applied to simulate the EOF in a polymer-coated nanopore.¹³ It is found that $r_{lc} = 40\sigma$ is a safe cutoff for our simulations. We choose $\sigma = \lambda_B$, where $\lambda_B = e^2/(4\pi\epsilon_0\epsilon_r k_B T)$ is the Bjerrum length (ϵ_r denotes the dielectric constant of the solvent). The Bjerrum length for water is 0.71nm at room temperature. The system temperature is controlled by a dissipative particle dynamics (DPD) thermostat^{31,32} with a friction coefficient $\gamma = 1.5\tau^{-1}$ and desired temperature $T = 1.2T^*$.³³ A more detailed description on the model potential can be found in Ref. 14. The positions and velocities of the particles are solved using the velocity-Verlet algorithm with a time step $\Delta t = 0.005\tau$. Initially, solvent particles and counterions are randomly dispersed within the simulation box. Grafted chains stretch normal to the wall of the channel. The nanoparticles distribute uniformly along the channel axis. The system is equilibrated for 3×10^5 time steps, and then an electric field is added for a further run of 2.5×10^5 time steps. After achieving a stable state, a production run of 6×10^5 time steps is performed to sample the simulation data.

III. RESULTS AND DISCUSSION

Figure 2(a) presents the distribution $P_n(r)$ of nanoparticles as a function of the distance r from the center of the nanochannel for systems MM, MP, MS, and RP. The grafting density is

FIG. 2. (a) Nanoparticle distribution function P_n and (b) counterion distribution function P_{ci} for the systems MM, MP, MS, and RP at $\rho_g \sigma^2 = 0.1$. The inset in (a) shows the average migration velocity.

fixed at $\rho_g = 0.1\sigma^{-2}$. The nanoparticles distribute near the wall of the channel for the system MP as seen from Figure 1(b). Moreover, they move in a very narrow region along the radial direction. This indicates that the nanoparticles are completely trapped within the polymer layer due to strong attraction between the brush and nanoparticles. We remind that the function $P_n(r)$ denotes the distribution of the center of nanoparticles. Therefore, the distribution function for the nearest position of the surface of nanoparticles from the wall of the channel corresponds to $P_n(r - r_n)$, that is, the profiles in Figure 2(a) should be shifted a distance of the radius r_n of nanoparticles. In the case of system MS, the swelling of the brush leads to the nanoparticles aggregate towards the center of the channel. Additionally, there is a wide range of the distribution profiles for systems MM and RP. It is clear that the distribution range of nanoparticles along the radial direction becomes wider for the system MM. This depends on a larger effective width of the channel due to the collapse of the brush under strong attractive interaction between polymer monomers. Changing the interparticle interaction (or the quality of the solvent) can control the effective size of the channel and further influence the flow velocity and fluid permeability.^{12,34}

We also give the average migration velocity of nanoparticles for four different systems in the inset of Figure 2(a). It is found that the nanoparticles are almost fully frozen within the brush in the case of system MP. The migration ability for the system MS is reduced compared to systems MM and RP. We attribute this to the shift of counterion distribution towards the center of the channel and the strong swelling of the brush. The distribution of counterions is shown in Figure 2(b). Clearly, the migration of more counterions towards the center for the system MS induces a strong drag force on them and nanoparticles. The attraction between monomers and solvent particles leads to the stretching of the brush. As seen in Figure 3, the ends of grafted chains almost reach the center of the channel for the system MS. Therefore, the nanoparticles are pushed away from the wall, further leading to they are confined in a narrow region as discussed above. Meanwhile, the friction between nanoparticles and end parts of polymer chains also becomes stronger. A further discussion on the counterion distribution (Figure 2(b)) and the monomer density (Figure 3) will be given below. Note that the migration velocity for the system RP is slightly higher compared to that in the case of system MM. Most nanoparticles for the system RP distribute in the region of $r < 4\sigma$. However, the nanoparticles in the case of system MM can be found in a wider region. It is worth emphasizing that the

FIG. 3. (a) Monomer density profiles ρ_m for the systems MM, MP, MS, and RP. The inset shows the brush thickness. (b) A snapshot of the system MM. For clarity, only polymer chains and wall particles are shown. Simulation data are obtained at $\rho_g \sigma^2 = 0.1$.

distribution of counterions exhibits a relatively small difference for systems MM and RP (Figure 2(b)). Therefore, each nanoparticle for the system MM will encounter more counterions on average. This leads to the nanoparticles suffer a stronger friction from the counterions which move in the opposite direction.

More counterions aggregate near the wall and the center of the channel in the case of system MS as shown in Figure 2(b). In the region of $4\sigma < r < 8\sigma$, the amount of counterions is reduced significantly. This is because the solvent-monomer attraction forces the counterions to migrate towards two sides of the brush. There are many counterions near the wall of the channel ($r < 7\sigma$) in the case of MP. The nanoparticles in the system MP are adsorbed into the brush layer, which leads to the translocation of counterions towards the grafting surface due to electrostatic attractive interactions. Though all nanoparticles are located in the brush and have a narrow distribution (Figure 2(a)), there are still a considerable amount of counterions that move away from the charged nanoparticles. This is a result of counterion diffusion because the binding ability of counterions to nanoparticles is not strong enough to condense or adsorb most counterions. Compared to the system MM, more counterions distribute in the center of the channel for the system RP due to its thicker brush.

Figure 3(a) shows the monomer density profiles for systems MM, MP, MS, and RP. Strong density oscillation can be observed near the wall. This reveals that the monomers are in an ordered arrangement along the direction normal to the wall. The polymer chains undergo a collapsed transition for the system MM. The monomer-monomer attraction results in the formation of compact aggregates. Therefore, the brush layer exhibits lateral inhomogeneity, or there exist lumps in the brush layer. Figure 3(b) gives a visual snapshot of the polymer layer for the system MM. Clearly, the polymer chains aggregate together to form different lump structures. These polymer aggregates are made up of grafted chains varying in the number from 5 to 30. Moreover, many surface patches among aggregates are bared. As a result, some nanoparticles have opportunity to contact with bared surface areas due to their free diffusion. As seen from Figure 2(a), the distribution profile for the system MM still exhibits an obvious nonzero value when $r > 6\sigma$. The scaling theory predicts that at moderate grafting densities the brush loses its lateral homogeneity and the grafted chains form aggregates.³⁵ For the system with longer grafted chains, the strong monomer-monomer interaction leads to the grafted chains aggregating to form pinned micelles with globular cores and extended legs connecting the core with the grafting site.¹² If increasing the grafting density to higher values, the surface of the compact polymer layer will become smoother. In contrast, the brush for the system MS is in a swelling state and the grafted chains are stretched away from the wall. Though the monomer-monomer and monomer-solvent interactions are the same for the MP and RP systems, the brush shows a slight swelling in the case of the MP compared to the system RP. The swelling of the brush is mainly caused by the binding of nanoparticles to the polymer chains. If the attracting nanoparticles have a much smaller size than the characteristic size of grafted chains (such as the radius of gyration), a collapsed conformation of the brush was observed.³⁶ To quantitatively analyze the thickness of the polymer layer for different systems, we also calculate the average thickness h of the brush by taking the first moment of the monomer density profile,

$$h = \frac{\int_0^R (R-r)\rho_m(r)rdr}{\int_0^R \rho_m(r)rdr}. \quad (1)$$

We present the brush thickness in the inset of Figure 3(a). The systems MM and MS correspond to the minimum and maximum brush thickness, respectively. The quantitative calculation indicates that the brush thickness for the system MP is larger than that for the system RP. These results obtained are in accordance with above discussion on the density profiles of monomers.

Furthermore, we address the effect of the grafting density on the distribution of nanoparticles. If not otherwise stated, the studied system refers to the system RP in the following

FIG. 4. (a) Nanoparticle distribution function P_n and (b) counterion distribution function P_{ci} of the system RP for different grafting densities.

discussion. Figure 4(a) shows the distribution profiles of nanoparticles as a function of the distance from the center of the channel at different grafting densities. At low grafting densities, the nanoparticles distribute in a wide range, and most of them are located near the wall of the channel. This indicates that the nanoparticles can penetrate into the brush layer in cases of sparse grafting. Additionally, with increasing the grafting density, such as $\rho_g \sigma^{-2} = 0.1$ and 0.2 , the nanoparticles are expelled from the polymer layer due to smaller free room in the brush and move towards the center of the channel. One can observe that at low grafting densities ($\rho_g \sigma^{-2} \leq 0.05$), the distribution profiles near the wall show strong oscillations. The oscillation behavior of nanoparticles is believed to be responsible for the distribution of counterions. As shown in Figure 4(b), there remain strong oscillations near the surface in the distribution profiles of counterions. The oscillation of distribution function for nanoparticles is related to the oscillation from counterions because of attractive interactions between them and nanoparticles. The oscillation at large r is a consequence of the layering of the counterions close to the wall and disappears upon approaching the center of the channel. When the grafting density is increasing to higher values $\rho_g \sigma^{-2} \geq 0.1$, many counterions still remain in the brush. Compared to nanoparticles with large size, the counterions are much easier to enter into the compact polymer layer.

Plotted in Figure 5 is the migration velocity of nanoparticles as a function of the grafting density. The velocity has a complex dependence on the grafting density. We presumably divide the velocity profile into six regions I–VI. At low grafting densities (region I), a decrease of the

FIG. 5. Average migration velocity u of nanoparticles for the system RP as a function of the grafting density.

migration velocity with increasing the grafting density is observed. In this range of grafting densities, a significant amount of nanoparticles distribute near the surface. Therefore, the friction effect between the chains and nanoparticles becomes stronger with the increase of the number of grafted chains per unit area. Then, there followed an increase of the velocity (region II). From the profiles of nanoparticle distribution (Figure 4(a)), the nanoparticles near the wall of the channel are reduced at $\rho_g \sigma^2 = 0.04$. This illustrates that more nanoparticles move away from the surface. Meanwhile, the distribution of counterions shows only a slight change (Figure 4(b)). So, the reduced friction between counterions and nanoparticles is a critical reason for the increase of the migration velocity in region II. Interestingly, further increasing the grafting density induces a slower translocation of nanoparticles (region III). One may note that there are a higher amount of nanoparticles near the wall (about $3.5\sigma < r < 5.5\sigma$) at $\rho_g \sigma^2 = 0.05$ than that in the case of lower grafting density $\rho_g \sigma^2 = 0.04$. Generally, this seems to be opposed to the fact that the increase of the grafting density leads to the migration of nanoparticles towards the center. Here, we want to point out that there tends to be migration towards the wall for the nanoparticles due to their free diffusion and attractive interaction from counterions near the wall. At $\rho_g \sigma^2 = 0.05$, the conformational entropy of the brush is more helpful to trap the nanoparticles into the brush. In the process of increasing the grafting density from $\rho_g \sigma^2 = 0.05$ to 0.1 (region IV), the polymer layer becomes more compact, which leads to a reduced free room within the layer. Consequently, more nanoparticles are expelled from the brush, and further the friction between the chains and the nanoparticles is weakened. This makes the nanoparticles move more rapidly along the channel direction. When the grafting density exceeds a certain critical value, the room in the polymer layer is inadequate to accommodate single nanoparticles. The contact area between the brush and the nanoparticles reaches a minimum, which yields much weaker friction. As a result, the migration velocity of nanoparticles is kept at a relatively stable maximum in region V. However, the effective diameter of the channel as the grafting density increases to higher values becomes smaller than the size of the nanoparticles (region VI). In this case, the drag force from the brush will be enhanced due to strong polymer-nanoparticle friction, and thus the translocation velocity also drops sharply. Additionally, at high grafting densities, such as $\rho_g \sigma^2 = 0.2$, many counterions are expelled from the brush and gather toward the center of the channel (Figure 4(b)). This can also suppress the translocation of the nanoparticles significantly.

Finally, we give the density profiles of brush monomers at different grafting densities in Figure 6. Undoubtedly, the monomer density increases upon increasing the grafting density, that is, the polymer layer becomes more compact.³⁷ As discussed above, this corresponds to a decrease of effective channel radius, which further pushes the nanoparticles towards the center of the channel. At the highest grafting density investigated ($\rho_g \sigma^2 = 0.2$), the grafted chains are in a strong extended state and the effective size of the channel is significantly reduced. The

FIG. 6. Monomer density profiles ρ_m of the system RP for different grafting densities. The inset shows the brush thickness as a function of the grafting density.

inset of Figure 6 illustrates the effect of the grafting density on the brush thickness. When $\rho_g \sigma^2 > 0.05$, we observe a linear dependence of the thickness on the grafting density.

IV. CONCLUSIONS

In conclusion, we examine how the interparticle interaction and the grafting density affect the transport dynamics of nanoparticles in a polymer brush-modified nanochannel. Our simulations indicate that the distribution and migration velocity of nanoparticles depend on the interparticle interaction significantly. In the case of system MS, the nanoparticles are pushed towards the center of the channel and confined in a narrow distribution region. The migration of nanoparticles is limited by the drag force from grafted chains and the distribution of counterions which are expelled towards the center. When there exist strong attractive interactions (system MP) between the nanoparticles and grafted chains, all nanoparticles are trapped into the polymer layer. The migration ability of nanoparticles is almost completely suppressed under the condition of fixed electric field studied. The binding of nanoparticles to the brush also causes a slight swelling of the brush. The polymer layer for the system MM is collapsed fully. Moreover, a wider distribution of nanoparticles is observed along the radial direction. It is found that the migration velocity in the case of system RP is somewhat higher than that for the system MM. We attribute this phenomenon to relatively strong counterion-nanoparticle friction. In this work, we note that the migration velocity of nanoparticles does not simply depend on the grafting density. The velocity is a complicated nonlinear function of the grafting density. To understand the irregular-looking migration behavior of nanoparticles, we presumably divide the velocity profile into six different regions. Finally, we can obtain a good understanding of the relation between migration velocity and grafting density by analyzing the counterion distribution, free room within the brush, nanoparticle-polymer friction, and brush configuration. Our results could provide a physical basis for further investigations into the role of polymer brush-modified surfaces in the transport of macroions such as various charged nanostructure and biomacromolecules. In the present simulations, the effects of the electric field, salt concentration, size, and surface charge amount of nanoparticles on the translocation behavior of nanoparticles have not been addressed. We will report a more detailed publication on the influences of these factors in the future.

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