Nanoparticle Flow in Polymer Grafted Channels

Sean Burgess, ‡ Kolattukudy P. Santo, ‡ Yefim Brun, ‡ and Alexander V. Neimark* ‡

‡ Department of Chemical and Biochemical Engineering, Rutgers, The State University of New Jersey, 98 Brett Road, Piscataway, New Jersey 08854, United States
‡ DuPont Central Research and Development, Wilmington, Delaware 19803, United States

Supporting Information

ABSTRACT: A better understanding of the specifics of nanoparticle transport through channels with polymer coated walls is of great importance for various biological, technological, and analytical processes. Here, we study flow of bare and ligand-functionalized nanoparticles in channels grafted with polymer brushes using dissipative particle dynamics. A dimensionless relationship is established between the ratio of the particle and solvent mean velocities and the scaling factor that equals the ratio of the particle size to the channel width reduced by the hydrodynamic thickness of a polymer brush. The simulated particle velocity profiles are found to be in agreement with experiments on the flow of polystyrene beads in hard-wall channels with the same scaling factor. The fact that the dimensions of particles and channels in simulations and experiments differed by 3 orders of magnitude confirms that the simulation results can be used to model experimental systems of larger size, in particular, nanoparticle separation on polymer coated chromatographic columns.

I. INTRODUCTION

Nanoparticle (NP) flow in channels grafted with polymer chains is important for many biological and technological processes, including membrane separations, fabrication of biomedical devices, sensors, and nanocomposites, colloidal stabilization, and motion induction of nano-objects and nanofluidics. Of practical relevance to NP flow in pore channels, are traditional analytical techniques of NP separations, such as field flow fractionation, size exclusion chromatography (SEC), and hydrodynamic chromatography (HDC). The modification of channel walls with polymer brushes (PB) greatly improves the precision of NP separation. The PB makes the pore wall “soft” and provides additional functionalities for NP selective adhesion and separation. While the general problem of nanofluidic separations and particle motion in pores with hard walls has been studied extensively both theoretically and experimentally, the specifics of NP flow in pores with soft PB-grafted walls remain unexplored. In this work, we study NP flow in PB-grafted channels by using dissipative particle dynamics (DPD) and determine the scaling relationship between the NP and solvent velocities, which depends on the geometrical parameters of the systems: effective dimensions of the channel, PB, and NP.

The traditional approach considers NP transport within the Poiseuille solvent flow in cylindrical or slit-shaped channels with smooth hard walls. While moving with the solvent, a hard particle is excluded from the near-wall slow-motion region at the distance equal to its radius, and experiences a slip along the walls. As shown by various theoretical methods and experimental confirmations, the average NP velocity, $\bar{u}_{NP}$, is related to the average solvent velocity, $\bar{u}_{solv}$, according to the following scaling equations, derived for slit-shaped and cylindrical channels, respectively

$$\frac{\bar{u}_{NP}}{\bar{u}_{sl}} = \left(1 + \lambda - Ci \frac{\lambda}{2}\right)^{-1}$$

$$\frac{\bar{u}_{NP}}{\bar{u}_{sl}} = \left(1 + 2\lambda - Ci \frac{\lambda}{2}\right)^{-1}$$

where the scaling factor $\lambda = R_{NP}/w_H$, the ratio of the effective NP radius to the channel hydrodynamic half-width/radius, $w_H$, and $C$ is an adjustment parameter, which depends on the particle and channel shape. In this work, we consider only spherical particles. In principle, this theory is extendable to nonspherical or penetrable particles like polymers in solutions where the particle radius is defined by its hydrodynamic radius.

With an intuitive yet incorrect supposition that a NP assumes the velocity of the solvent at the position of the NP center of mass, one easily comes to equation 1 with $C = 1$, by integrating the parabolic velocity profile in the limits of $\pm (w_H - R_{NP})$. In practice, the values of $C$ do not equal 1, and the NP lags behind the solvent due to a variety of affects, most predominantly, NP rotation caused by the inhomogeneous solvent flow and interaction of the NP with the wall. The parameter $C$ is used to account for this lagging affect. To explain how the NP flows and rotates in a channel, the problem is often split up in to two parts: NP flow in the center of the channel far from the channel wall and NP flow near the channel wall. When the NP flows in the channel far from the wall, the solvent velocity across its diameter is not constant; solvent velocity on the NP edge closest to the wall is slower.
than that farther from the wall. This causes the NP to rotate, creating a slowing effect. When the NP flows near the channel wall, the rotation and, consequently, the slowing effect, becomes more pronounced. When flow in infinitely long cylindrical channels with hard walls was considered, the theoretical work by Brenner and Gaydos31 suggested C ≈ 4.9 for hard impermeable spheres which was further confirmed experimentally.35 Staben et al.37 theoretically derived an equation for the particle velocity profile in a slit pore with hard walls, which was experimentally confirmed in the subsequent work by Staben and Davis28 on polystyrene spheres. Their results are fulfilled (eq 1a) with the parameter C ≈ 2.6. More complex models exist which consider higher order correction terms to equation 1,26–31 however, within the precision of the present study, accuracy between the models cannot be assessed. Dechadilok and Dean29 provide an in depth discussion of these various models and their differences. It is important to note that in the case of a soft particle, e.g. polymer coils and globules, the value of C is significantly smaller compared to solid particles, as predicted by theory and experiment alike.15,22,24–26 For example, DiMarzio and coworkers24–26 have shown that C ≈ 2.7 for dilute polymer solutions in cylindrical channels, a widely accepted value which has been experimentally verified.35,36 Recently, Korolev et al.32 experimentally measured the velocity of polystyrene standards in capillary columns, finding C = 2.4.

In the case of packed bed columns, eq 1b is commonly employed with the effective hydrodynamic channel width, which is equal to the diameter of the cylindrical channel having the same surface to volume ratio as the column.15,32,33 The value of parameter C depends on the column structure and the nature of particles. Tijssen et al.33 recommend, based on empirical evidence, the value of C ≈ 2.7 for calculating the elution time of polymeric coils in HDC. Stegeman et al.34 studied the flow of polystyrene standards in packed bed columns. The columns were packed with nonporous beads of size 1.4, 1.9, and 2.7 μm. The authors found C ≈ 3.7 best fit the data across the packed bead size. Appreciable differences are found in monolith columns. In comparison to packed bed columns, monolith columns have a more regular channel structure.35 Edam et al.36 studied the flow of polystyrene standards through polymer based monolithic columns. While they do not conclude which value of C is most suitable, from the figures presented, it appears that the value of C slightly smaller than 2.7 would best fit their data.

The authors of the present study recently considered adhesion and separation of bare and functionalized NPs on polymer grafted substrates.17,18 It was shown that by varying the composition of the binary mixture of thermodynamically good and poor solvents, it is possible to control the PB conformation and regulate the conditions of solvent flow and NP adhesion. Using dissipative particle dynamics (DPD) simulations of slit-shaped channels, it was shown that solvent within the bulk of the PB is stagnant, and the solvent velocity in the central part of the channel outside the PB can be approximated by a parabolic Poiseuille profile with the diminishing velocity at the distance to the channel wall that equals the hydrodynamic width of PB, \(w_{PB}\):

\[
u(z) = \frac{3}{2} R_{slit} \left(1 - \frac{z}{w - w_{PB}}\right)^2
\]

where z is the coordinate across the channel with the origin in the channel center. The hydrodynamic width, \(w_{PB}\), characterizes the extension of the PB and separates, using the chromatographic terminology, the mobile and stationary phases. \(w_{PB}\) depends on the solvent quality, PB density, and chain length. Equation 2 implies that solvent flow in a PB-grafted channel of half-width, \(w\), resembles solvent flow in the channel with hard walls of the effective half-width, \(w_{PB}\), reduced by the PB hydrodynamic thickness, \(w_{PB} = w - w_{PB}\). It was shown that for bare NPs, the mean NP velocity complies with eq 1a with \(C = 2.7\) for dilute polymer solutions in cylindrical channels, a widely accepted value which has been experimentally verified.35,36 Recently, Korolev et al.32 experimentally measured the velocity of polystyrene standards in capillary columns, finding C = 2.4.

II. COMPUTATIONAL METHODS

We use the DPD model employed in our earlier works17,18 to simulate the flow of bare and ligand-functionalyzed NPs in PB-grafted channels using DPD, the coarse-grained method found efficient for modeling NP-PB systems in our earlier works17,18,37,58 as well as the works of others.30–34 We calculate the NP velocity profiles and conclude that similar to the solvent flow, NP flow in PB-grafted channels resembles NP flow in the hard-wall channels of the effective size reduced by the hydrodynamic thickness of the PB. This conclusion is confirmed by the experimental data of Staben and Davis.28 We find that for bare NPs, the mean NP velocity complies with eq 1a with parameter C ≈ 2.6 in agreement with findings of Staben et al.27,28 At the same time, the flow of ligand functionalyzed NPs is characterized by a lower parameter, C = 2.2. Our findings suggest a practical methodology of extension of the equations adopted in HDC on hard-wall substrates to soft-wall substrates; the effective channel size has to be reduced by the hydrodynamic thickness of the PB. This conclusion has important practical implications for the chromatographic separation of functionalized NPs on polymer-grafted substrates.

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channel walls, the system density is taken to be equal to 3 beads/$R_c^3$ which also corresponds to the density of liquid solvent (benzene) at ambient conditions.

The lateral size of the simulation system, $28.4 \times 28.4$ nm² and $56.8 \times 56.8$ nm² for 2.84 and 5.68 nm NPs, respectively, is chosen to avoid the effects of periodic boundary conditions. Hydrodynamic channel half-width is varied from 3.7 to 57 nm to screen a wide range of scaling parameter, $\lambda = R_{NP}/w_{PB}$ (from 0.1 to 0.75). The largest system considered contains 3,353,600 beads to which Newton equations of motion are applied to monitor the system evolution to a steady state. The simulations start with a NP placed at different initial distances from the pore center. A constant force is applied to all NP positions. The driving force is varied depending on the channel width to provide the maximum solvent velocity within $0.1R_c/\tau < u_{max} < 0.4R_c/\tau$. After the steady state is reached, in order to ensure sampling of the whole velocity profile across the channel, a set of parallel simulations is performed with the NP placed at different initial positions. The first 10% of the data gathering steps are ignored to ensure that the system reaches the steady state; then data is collected for the remaining 900000 steps. Newton’s equations of motion are solved using the Velocity-Verlet algorithm employed in an NVT-ensemble. All simulations are run with LAMMPS using the XSEDE Comet resource. Further simulation details are given in the Supporting Information, Sections I and II.

### III. RESULTS AND DISCUSSION

For all systems studied, we confirmed the validity of the parabolic approximation eq 2 for the solvent velocity. We deal here with a good solvent, which penetrates into the interior of the PB and remains stagnant within the distance of $w_{PB}$ from the solid wall. The flow of solvent in the PB-grafted channel of the width $w$ is similar to that in a hard-wall channel of the effective hydrodynamic radius (half-width) reduced by the hydrodynamic width of PB, $w_{eff} = w - w_{PB}$. In the case shown in Figure 1, $w_{eff} = 27.9$ nm for the channel of $w = 34.1$ nm. The value of the hydrodynamic width of PB, $w_{PB}$, is determined from the fitting of the computed solvent flow profile to the Poiseuille parabolic approximation as the distance from the channel wall when the velocity vanishes. The PB hydrodynamic thickness, $w_{PB}$, increases with the increases of PB density and the chain length. For example, the PB hydrodynamic width equals $w_{PB} = 6.2$ nm at 2.4 chains/nm² (shown in Figure 1) and $w_{PB} = 3.3$ nm at 0.6 chains/nm² with same chain length of 15 beads/chain (Figure S2).

Simulating the NP flow, we come to a similar conclusion that NP flow in a soft-wall channel resembles the NP flow in a hard-wall channel with reduced (by the hydrodynamic width of PB) radius, $w_{eff} = w - w_{PB}$. This is illustrated in Figure 2. The collection of blue points represents instantaneous velocities of NPs sampled in the course of DPD simulations. NPs are confined to the central mobile zone of the channel, expelled from the PB hydrodynamic boundary by its radius, Figure 2 (left). Due to Brownian diffusion induced by the pairwise Langevin thermostat, the thermal fluctuations of NP velocities are distributed with respect to the Boltzmann distribution centered around the mean NP velocity. Figure 2 (right) shows this distribution for the NP velocities sampled around the pore center. At the same time, the NP velocity, averaged along these fluctuations (depicted by the red line) is approximated by a parabola, which terminates at the boundary of the mobile zone $z_m = \pm (w_{eff} - R_{NP})$ with a certain slip velocity. The simulations show that NPs rotate in nonuniform solvent flow and lag behind the solvent. Of course, the PB surface is soft, so that NPs fluctuate and partially penetrate beyond the mobile zone boundary $z_m$. However, the analysis of the statistics of NP locations shows that the deviation between $z_m$ and the farthest distances from the pore center achieved by NP due to radial

![Figure 1](image1.png) **Figure 1.** Simulation setup for modeling NP flow in PB-grafted channels. PB (tan) is attached to the plain solid immobile substrate (light blue) with a certain density (here, 2.4 chains/nm², chains consist of 15 beads). Solvent not shown. PB density profile is shown in red. The solvent velocity profile (broken blue line) is approximated by a parabolic Poiseuille profile with vanishing velocity at the distance to the wall that equaled the hydrodynamic thickness, $w_{PB}$, of PB (vertical dotted black line, here, $w_{PB} = 6.2$ nm).

![Figure 2](image2.png) **Figure 2.** Example of simulated NP velocity profile of 2.84 nm NP in the PB-grafted channel of hydrodynamic half-width of 6.46 nm (left). Blue points represent the instantaneous NP velocity samples along the simulation run. The black and red lines represent, respectively, the averaged solvent and NP velocity profiles fitted by the parabolic approximation. The purple dotted vertical lines mark the pore wall. The distribution of instantaneous NP velocities is shown for the pore center (right). The solid line corresponds to the expected Maxwell–Boltzmann distribution centered at the averaged NP velocity in the solvent flow.
diffusion is negligibly small, see Supporting Information, Section III.

In Figure 3 (left), we compare the results of our simulations of NP flow in the systems with different scaling factors, $\lambda = R_{NP}/w_{H}$, to the experimental data of Staben et al.28 on the particle flow in slit channels with hard walls. The data is presented in reduced units: velocities are normalized by the maximum solvent velocity in the pore center, and z-position across the channel is normalized by the halfwidth, $w$, of the channel with hard walls (experimental data) and by the hydrodynamic halfwidth, $w_{H} = w - w_{PB}$ (simulated data). Taking into account the huge difference of scales involved in simulations (NP size <12 nm, channel width <120 nm) and experiments (NP size >36 $\mu$m, channel width >500 $\mu$m) the agreement is impressive. It shows that that this scaling works over 3 orders of magnitude, and thus, the results of simulations performed on the nanoscale level can be employed for making quantitative predictions for practical systems of significantly larger scales. This is specifically important for modeling chromatographic columns with hierarchical pore structures ranging from tens of micrometers down to several nanometers.

Figure 3 (right) presents the simulated mean NP velocity across the PB-grafted channels normalized by the average solvent velocity as a function of the scaling factor, $\lambda$, in comparison with the experimental data and theoretical predictions (broken line) of Staben et al.27,28 for hard-wall slit-shaped pores. This representation is useful for analyzing the chromatographic separation as the ratio of the mean velocities is reciprocal to the ratio of the respective retention times. Noteworthy, the data presented are reasonably approximated by eq 1a with the parameter $C = 2.6$, shown as the dotted black line. The apparent deviation of the experimental points from the theoretical curve at the smallest $\lambda$ was explained by the authors28 by the specifics of the channel entrance construction in their experimental setup. Agreement with the simulated data is within the accuracy of experimental data.

Figure 4 presents the difference between the normalized (with respect to the maximum solvent velocity) velocity profiles for the solvent (black), bare NPs (red), and functionalized NPs (blue) for different values of the scaling factor $\lambda$. All velocities are normalized with respect to the maximum solvent velocity in the pore center.
with the solvent and the surface exclusion effect bears the first order contribution of $\lambda$ into eq 1a. As $\lambda$ increases, the distinction between the solvent and NP velocities becomes more and more apparent. The normalized velocity of ligand-functionalized NP is slower than that for the bare NP at the same value of $\lambda$ due to the enhanced friction between grafted chains, PB and solvent, which intensifies NP rotation. The effective radius of functionalized NPs is 1.18 nm larger than that of their bare counterparts. This fact causes a smaller width of the mobile zone sampled by functional NPs visible in Figures 4.

In Figure 5, the relationship between the NP residence time, $\tau$, and the scaling factor, $\lambda$, is presented in the coordinates employed for the analysis of NP separations in HDC. The NP residence time, $\tau$, is given here in reduced units as the inverse of the mean NP velocity with respect to the mean solvent velocity. As observed in Figure 5, when $\lambda$ is small, the residence time decreases as $\lambda$ increases. This is due to the exclusion of the NP from the slower flow zone. However, as $\lambda$ increases further, the residence time begins to increase due to the enhanced residence time as the inverse of the mean NP velocity. This independence suggests that the NP flow in polymer-grafted channels of other shapes (cylindrical, within packed bed and monolith columns) is similar to the NP flow of the hard-wall channels of effective radius reduced by the PB hydrodynamic width. This conclusion brings about an important practical recommendation: to model NP separation on polymer-grafted capillaries and columns grafted with polymers, one may use the models employed for hard-wall channels, like eq 1b, with the effective channel radius reduced by the PB hydrodynamic width.

**IV. CONCLUSIONS**

In conclusion, we show that the NP flow in soft-wall polymer-grafted channels is similar to that in hard-wall channels of effective radius, reduced by the PB hydrodynamic width. Using the scaling factors, $\lambda = R_{np}/w_H$, agreement is found between the simulated and experimental data for NPs and channels that differ in size by 3 orders of magnitude. This agreement confirms that the results of simulations can be used to model experimental systems of larger dimensions. The PB hydrodynamic width, which determines the boundary between mobile and stationary phases in polymer-grafted channels, is determined by the solvent quality and does not depend appreciably on the channel shape and intensity of solvent flow.7,18 This independence suggests that the NP flow in polymer-grafted channels of other shapes (cylindrical, within packed bed and monolith columns) is similar to the NP flow of the hard-wall channels of effective radius reduced by the PB hydrodynamic width.


