Modeling confined nanoparticle transport through post arrays with Lagrangian particle tracking

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Abstract

Recent experiments show that nanoparticles flowing through strongly confining quasi-2-D nanopost arrays exhibit early breakthrough, reminiscent of the behavior observed in complex 3-D porous media. Inspired by these experiments, we develop a minimal computational model based on Lagrangian particle tracking (LPT) to simulate the flow-driven transport of finite-sized nanoparticles through 2-D nanopost arrays. This minimal computational model, which neglects time-dependent fluctuations in fluid flow, provides semi-quantitative predictions of several key particle transport properties. The average velocity along the flow direction and the longitudinal dispersion coefficients computed from the LPT simulations are in semi-quantitative agreement with experiment. The transverse dispersion coefficients from the LPT simulations, however, are larger than those found in experiments, likely due to transient attractions between the particles and the nanoposts that are not modeled in the simulation. We describe in detail the successes and shortcomings of the model, along with promising avenues for future improvement.

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I. INTRODUCTION

Understanding the transport of nanoparticles through geometrically complex porous media is a problem with widespread implications in chemical engineering. Nanoparticles synthesized in solution, for example, are separated and purified through gel electrophoresis [1], size-exclusion chromatography [2], or membrane [3] processes, requiring particles to be transported through small channels or pores in gels, columns, or membranes. Nanoparticles used to enhance oil recovery [4], by modifying the viscosity of sweep fluids [5] or the wetting properties of nearby interfaces [6, 7], must be transported to regions of low permeability within reservoirs. Similarly, the effectiveness of therapeutic nanoparticles depends on their ability to transport through narrow blood capillaries [8] or penetrate deep into tumors [9, 10]. Finally, controlling the spatial distribution of nanoparticles flowed into confined geometries [11], arising as one example during infiltration into a fiber matrix [12], is required to attain the exceptional functional or mechanical properties of particle-laden nanocomposites [13]. In each of these applications, the particle size is comparable to the confining length scale, such as a pore or throat diameter. Hence, designing processes to deliver particles deep within a porous medium requires methods to predict particle transport from the geometry of the medium.

Particle transport in a disordered medium has been traditionally described through macroscopic parameters such as tortuosity, porosity, and pore connectivity [14, 15]. Both molecular diffusive and advective processes contribute to asymptotic (long-time) dispersion, and the relative contribution from each process is determined by the Péclet (Pe) number, the ratio of the rates of advective and diffusive transport. When particles are small compared to characteristic length scales within the medium, asymptotic dispersion is controlled by molecular diffusion when Pe is small and by advection when Pe is large [16]. Particle velocity profiles at the pore scale reflect the local spatial heterogeneity, [17] but do not affect asymptotic dispersion when Pe is large [18]. The use of macroscopic geometric parameters relies on the assumption that the disordered structure of the medium uniformly mixes the fluid [14], such that the particles fully sample the void space within the medium [19]. If, instead, particles cannot fully sample the void space, deviations from this picture can arise. Particles flowed through ordered media, for example, may follow deterministic [20, 21] or time-periodic [22] trajectories, so that transport is intimately coupled to geometry. Likewise,
particles whose size is close to that of channels or voids in the medium may be excluded from accessing slow streamlines near surfaces [23]. As one consequence, particles move through the medium more rapidly and exhibit ‘early breakthrough’ relative to tracers [24, 25]. These examples suggest that, in many scenarios, developing insight into the controlling physics [26] requires methods to link the pore-scale behavior to macroscopic transport.

Our recent experiments explore the transport properties of particles that are strongly confined within quasi-2-D porous media [27–29]. These media consist of dense, periodic arrays of high-aspect-ratio nanoscale posts of diameter 500 nm and height 10 µm that are fabricated within silicon microchannels. In one experiment, particles of diameter 400 nm were transported at low Reynolds numbers (Re ≤ 10^{-4}) through arrays of nanoposts, spaced by 0.8 – 2 µm and aligned with an open channel along the direction of flow. The particles in these experiments exhibited coupled diffusive and advective transport processes [28]. The strong confinement imparted by the closely-spaced nanoposts altered the dispersion of particles within the arrays, as particles were constrained to the relatively fast streamlines near the center of the channels defined by the nanoposts. Although this result suggests that confinement may promote the early breakthrough often observed in 3-D porous media, which physical mechanisms control this process at the pore-scale remains poorly understood.

Inspired by these experiments, we develop a minimal computational model based on Lagrangian particle tracking (LPT) [30–33] to describe flow-driven particle transport through nanopost arrays. Lagrangian particle tracking simulates the motions of tracer particles subjected to stochastic Brownian forces from thermal fluctuations and viscous drag arising from a fluid flow field [31]. Although the fluid flow field varies spatially throughout the systems, it is assumed to be time-independent and unaffected by the presence of the tracer particles. Thus, LPT models momentum transfer from the fluid to the particles via viscous drag, but it neglects momentum transfer from the particles to the fluid. More rigorous methods for simulating hydrodynamic interactions such as Stokesian dynamics [34, 35] and stochastic rotational dynamics [36, 37] have been developed and successfully applied to study particle dynamics in bulk suspensions and confined systems [38–42]. They are computationally intensive, however, and challenging to apply to model flow through geometrically complex media. Additionally, it is not clear a priori that a detailed description of hydrodynamic interactions is necessary to capture experimentally observed trends in long-time particle transport behavior.
Here, we investigate LPT as a computational approach for modeling particle transport in strongly confined media. We propose a simple extension to LPT to model the transport of finite-sized particles through highly confined systems where the flow field varies over length scales comparable to the particle size. This minimal computational model, which neglects time-dependent fluctuations in fluid flow and physicochemical interactions between the particles and the posts, semi-quantitatively reproduces several key transport properties of particles in nanopost arrays. Both morphological measures of the trajectory shape (such as tortuosity and angular correlations) as well as the distributions of velocities in the longitudinal and transverse directions are in semi-quantitative agreement with the experiments in Ref. [28]. Although the transverse dispersion coefficients computed from the LPT particle trajectories slightly over-predict experimental estimates [28] due to the absence of attractive particle-post interactions in the model, the longitudinal dispersion coefficients are in good agreement with experiment. These promising results suggest that the minimal LPT model proposed in this study can be extended in future investigations aimed at understanding the role of medium geometry and flow conditions on the transport behavior of strongly confined nanoparticles.

II. METHODS

Post arrays have been used in both experiment and simulation as model porous media with well-controlled properties (e.g., confinement length, structural order, and surface chemistry) for developing fundamental understanding of processes ranging from capillary wetting to polymer translocation [43–48]. Our recent fluorescence microscopy experiments, for example, have probed the flow-driven transport of polystyrene nanoparticles suspended in water through ordered arrays of silicon nanoposts fabricated using electron beam lithography [27–29]. Here, we develop a minimal computational model for predicting nanoparticle transport through nanopost arrays. The proposed computational model can be extended to study particle transport in arbitrarily complex arrangements of nanoposts. For the purpose of validating our modeling, however, we restrict our current investigation to the simplest geometry in which the nanoposts are arranged on a regular square lattice with edge length \( a \) (Fig. 1(a)). Although the posts in the experimental realization of this system have finite length along the \( z \)-axis, the laminar fluid flow (\( \text{Re} \approx 10^{-3} \)) entrains the particles in a
near-constant vertical $xy$-plane. We therefore model the system as 2-D and only consider particle motions and variations in fluid flow in the $xy$-plane (Fig. 1(a)). The confinement length for this system is the edge-to-edge distance between posts $S = a - d_p$, where $d_p$ is the post diameter. This quantity, along with the diameter of the transported nanoparticles $d_{np}$, defines the dimensionless confinement parameter $\zeta = d_{np}/S$.

Flow-driven particle transport through the model nanopost arrays is simulated by using LPT in conjunction with the Lattice-Boltzmann (LB) method [49, 50]. In this approach, LB is used to calculate the steady-state velocity fields that develop inside the nanopost arrays in response to uniform flow imposed at the boundary. The LPT algorithm is then used to simulate diffusion and advection of particles through the nanopost arrays in the predetermined LB velocity fields [31]. The motion of each particle is described by the Langevin equation:

$$m_{np} \frac{d^2 r_{np}(t)}{dt^2} = F_B(t) + F_D(t), \quad (1)$$

where $t$ is time, $r_{np}$ is the particle’s position vector, $m_{np}$ is the particle’s mass, and $F_B$ and $F_D$ are the Brownian and drag forces acting on the particle, respectively. The Brownian force is chosen to satisfy fluctuation-dissipation, which requires that $\langle F_{Bi}(t) \rangle = 0$ and $\langle F_{Bi}(t) F_{Bj}(t') \rangle = 2k_B T f_{ij} \delta(t - t')$, where indices $i, j$ denote components of the force, $k_B$ is Boltzmann’s constant, $T$ is temperature, $\delta(t - t')$ is the Dirac delta function, $\delta_{ij}$ is the Kronecker delta, $f = 3\pi \mu d_{np}$ is the friction coefficient, $\mu$ is the fluid viscosity, and the angular brackets denote ensemble averages. These requirements are satisfied by computing each component of the Brownian force using

$$F_{Bi} = \sqrt{\frac{2k_B T f}{\Delta t}} \xi_i, \quad (2)$$

where $\Delta t$ is the integration time step and $\xi_i$ is a standard Gaussian random variate. The drag force is evaluated using

$$F_D(t) = f(U - v_{np}(t)), \quad (3)$$

where $U$ is the local velocity of the fluid and $v_{np}(t) = \frac{dr_{np}(t)}{dt}$ is the particle’s velocity. Forces between particles are neglected due to the dilute conditions of the suspension.

The LPT-LB approach has been successfully applied to simulate the transport of tracer particles in systems ranging from packed beds to tissue scaffolds [31, 32]. The principal assumption underlying LPT is that the velocity field is unaffected by the presence of the
FIG. 1. (a) Nanopost array model used in this study. The fluid flow field is rendered using the gradient background. (b) The drag force (Eq. 3) is evaluated using the mean fluid velocity computed by averaging values of local velocity (arrows) at evenly spaced points on the particle's surface. Eight points are shown in the schematic; thirty points are used in the simulations. (c) Example particle trajectories for a flow rate of $Q = 0.05 \mu$L min$^{-1}$ and a post spacing of $S = 1 \mu$m.

particles, which is only valid for infinitesimal tracers [31]. This assumption can be relaxed
by using more sophisticated particle-fluid coupling schemes in which the LB equations and particle equations of motion are solved simultaneously [51, 52]. These schemes are significantly more computationally demanding, however, which frustrates simulation of long-time behavior relevant to making comparison with experiment. For the purpose of the current study, the simple and computationally inexpensive LPT coupling scheme serves as a starting point for developing a minimal computational model for simulating particle transport through nanopost arrays. Further, although the LPT coupling scheme is expected to break down to some extent for finite-sized particles in highly confined geometries, we show that this minimal modeling approach yields semi-quantitative agreement with experiment in predicting particle transport behavior. Consequently, we leave investigation of more rigorous and computationally demanding particle-fluid coupling schemes for future studies.

We used the standard D2Q9 LB model [53, 54] to obtain the 2-D fluid velocity profile inside the model nanopost arrays. The dimensions and physical parameters for the system were chosen to match the experiments reported in Ref. [28]. The LB equations were solved for a periodic unit cell containing a single post with diameter $d_p = 500$ nm using a node spacing of 25 nm. The nanopost was modeled as an impenetrable solid by setting the fluid distribution in the interior nodes to zero, and a no-slip boundary condition was enforced at the solid-fluid interface using the bounce-back method [53, 54]. The lattice constant of the unit cell was adjusted to vary the edge-to-edge post spacing $S$ from 0.8 to 2 $\mu$m, which is the same range investigated in experiment. Physical properties of the LB fluid were set equal to those of water at 25 $^\circ$C. Flow in the positive $x$-direction was generated by imposing a uniform velocity profile at the $x = 0$ boundary of the unit cell. The magnitude of the velocity at the boundary was chosen to approximately match the experimental flow conditions. For a given flow rate $Q$, the boundary velocity was set equal to the superficial velocity $U_s = Q/A$ estimated from cross-sectional area $A$ of the micro-channel system described in Ref. [28]. The steady-state velocity profile was computed by carrying out the LB simulations until the velocity at each node converged within a tolerance of 1 part in $10^5$ between subsequent iterations.

The steady-state velocity profiles from the LB calculations were used in conjunction with LPT to simulate diffusive-advection particle transport through the model nanopost arrays. The particle equations of motion (Eq. 1) were solved numerically using a forward Euler integration scheme [55]. An appropriate integration time step $\Delta t$ was identified by
performing regression analysis under quiescent conditions \((i.e., Q = 0)\). Key properties of the system \((e.g.,\) particle displacement distributions) were computed from simulations performed using values ranging from \(\Delta t = 10^{-2}\) to \(10^{-8}\) s. The computed properties were statistically indistinguishable for choices of \(\Delta t \leq 10^{-4}\) s. Thus, we conservatively chose \(\Delta t = 10^{-5}\) s for our production runs. Although this choice of \(\Delta t\) is suitable for simulations performed under quiescent conditions, the time step must be decreased to achieve comparable accuracy in integrating the equations of motion in the presence of fluid flow. Specifically, \(\Delta t\) should vary as \(Pe_x^{-1}\), where \(Pe_x = \frac{V_x d_{np}}{D_q}\) is the Péclet number, which is defined in terms of mean particle velocity in the direction of flow \([17, 56]\), \(\nabla x\), and the particle diffusivity in the nanopost array under quiescent conditions, \(D_q\). Consequently, we used values of \(\Delta t\) ranging from \(10^{-5}\) to \(10^{-7}\) s under the flow conditions examined in this study.

In standard LPT implementations, the drag force is computed using the fluid velocity \(U\) at the particle’s center \(r_{np}\) \([31–33]\). Although this approach is suitable for infinitesimal tracers, it neglects variations in the fluid velocity that occur across finite-sized particles. As a result, we used an alternative scheme in which \(U\) was replaced with the mean fluid velocity \(\bar{U}\) computed by averaging the values of \(U\) at 30 evenly distributed points on the particle’s surface (Fig. 1(b)). Following experiment, the particle diameter \(d_{np}\) was set to 400 nm and the mass \(m_{np}\) was chosen to match the density of polystyrene (1.050 g cm\(^{-3}\)). Interactions between the particles and nanoposts were treated as elastic collisions. Each particle trajectory was propagated for 20 s using LPT, and particle statistics for each system were computed by averaging properties over at least 100 independent single-particle trajectories.

### III. RESULTS AND DISCUSSION

#### A. Pore-scale trajectories

The experiments reported in Ref. [28] examined a range of flow rates and confinements that spanned the crossover from diffusion-dominated to advection-dominated transport, indicated by changes in trajectory shape. Thus, we first characterize the morphology of the trajectories of nanoparticles in nanopost arrays obtained using the LPT simulation with two metrics describing the loss of directional persistence: the average tortuosity \(\langle \tau \rangle\) and the average of the cosine of the angle between velocity vectors \(\langle \cos \chi \rangle\). The long-time limit of
the average tortuosity \( \langle \tau \rangle \) sharply decreases as the Péclet number is increased (Fig. 2(a)), indicating that the trajectories of the nanoparticles transported through the model nanopost array become increasingly linear. Likewise, the average angle between consecutive velocity vectors, calculated over a time interval of 0.1 s, increases from near-zero at low Pe\(_x\) to a near-constant value of 0.8 at high Pe\(_x\) (Fig. 2(a)). This increase is consistent with a transition from diffusion-dominated transport at low Pe\(_x\), for which the directions of the instantaneous velocities are expected to be essentially uncorrelated, to advection-dominated transport at high Pe\(_x\), for which the velocity vectors are expected to be strongly directionally correlated. At the highest flow rate, this transition shifts to slightly higher Pe\(_x\) in simulation. This discrepancy with experiment suggests that the collisions between the nanoparticles and nanopost are too elastic in simulation, which slightly enhances decorrelation of the particle velocities in highly confined post array systems at high flow rates. Nevertheless, both the values of \( \langle \tau \rangle \) and \( \langle \cos \chi \rangle \) are in reasonable agreement with the values obtained in the experiments of Ref. [28].

To investigate the effect of confinement on particle transport, we next examine the probability distribution \( P(V_x) \) of velocities along the direction of flow (\( V_x \)) (Fig. 3(a)). The velocity distribution \( P(V_x) \) is approximately Gaussian when the posts are spaced relatively far apart and the confinement parameter \( \zeta = d_{np}/S \) is small (e.g., \( \zeta = 0.2 \)). Under these conditions, the maximum in \( P(V_x) \) coincides with the average advective velocity of the particles. As the extent of confinement increases, however, the maximum in \( P(V_x) \) shifts to lower values of \( V_x \) due to the obstruction of particle transport by the nanoposts. A similar trend is also observed in the particle velocity distributions measured in experiment under comparable flow conditions[57] (Fig. 3(b)).

In both simulation and experiment, the longitudinal velocity distributions become increasingly non-Gaussian and asymmetric as the extent of confinement increases (Fig. 3). This behavior arises due to an increase in the probability that particles will become temporarily trapped inside cages formed by adjacent nanoposts. This caging effect leads to an increase in \( P(V_x) \) near \( V_x = 0 \). Hence, the asymmetry of the \( V_x \) distributions reflects a competition between two distinct processes: advection along streamlines and caging inside the interstices. Additionally, the experimental \( V_x \) distributions for the highly confined systems (\( \zeta = 0.37 \) and \( 0.49 \)) exhibit a strong peak near zero. We posit that this behavior is due to enhanced caging resulting from weak, short-range attractions (\( \ll d_{np} \)) between the particles.
FIG. 2. (a) Average tortuosity $\langle \tau \rangle$ and (b) average angle between velocity vectors $\langle \cos \chi \rangle$ as a function of $\text{Pe}_x$. Flow rates are indicated in the legend. Closed symbols: simulation; open symbols: experimental data from Ref. [28].

and nanoposts in the experimental system. This hypothesis is consistent with the fact that caging peak is significantly weaker in simulation, where the particle-post interactions are treated using a purely repulsive, elastic collision model. Although short-range, attractive interactions can in principle be implemented in simulation, they cause the particle equations of motion to become stiff. To compensate for increased stiffness, the integration time step must be decreased by more than ca. 5 orders of magnitude, which increases the computational cost of the simulations by the same factor. Further, the particle-post interactions have not been characterized in the experimental system and thus the range and strength of the attractions is not accurately known. Consequently, we have omitted attractions from the minimal model reported here and leave systematic investigation of the effects of such
FIG. 3. Probability distribution of particle velocities in the longitudinal direction obtained in (a) simulation and (b) the experiments reported in Ref. [28] acquired at a flow rate $Q = 0.05 \mu$L min$^{-1}$. Values of the dimensionless confinement parameter $\zeta$ are indicated in the legends.

interactions on particle transport for future studies in which we will present efficient LPT algorithms to handle short-range attractions. We note that in limited test cases where attractive particle-post interactions were modeled, however, we observe enhanced caging and a more pronounced peak near zero in the $V_x$ distributions computed for highly confined systems (not shown).

The probability distribution $P(V_y)$ for the transverse particle velocity ($V_y$, velocity perpendicular to flow) from simulation is symmetric and approximately Gaussian when the confinement parameter $\zeta$ is small (Fig. 4(a)). The distributions $P(V_y)$ become increasingly narrow and non-Gaussian as $\zeta$ increases, however, due to caging of the particles in the array interstices. This effect is significantly more pronounced in experiment (Fig. 4(b)), which can
again be attributed to enhanced caging due to post-particle interactions. In both simulation and experiment, $P(V_y)$ remains symmetric regardless of the extent of confinement or flow conditions. As a result, the average transverse velocity $\overline{V}_y$ is zero in these systems, which is a consequence of the absence of flow along the $y$-direction.

![Graph showing probability distribution of particle velocities in the longitudinal direction](image)

**FIG. 4.** Probability distribution of particle velocities in the longitudinal direction obtained in (a) simulation and (b) the experiments reported in Ref. [28], acquired at a flow rate $Q = 0.05$ $\mu$L min$^{-1}$. Values of the dimensionless confinement parameter $\zeta$ are indicated in the legends.

**B. Particle transport and dispersion**

The results reported in Figures 2 – 4 show that the trajectories obtained by simulation are in near-quantitative agreement with the experiments reported in Ref. [28]. To link the pore-scale trajectories to particle dispersion, we first calculate the average advection velocity $\overline{V}_x$ from a linear fit to the average particle displacement as a function of time. The simulations
predict that the average longitudinal particle velocity $V_x$ will decrease monotonically as the extent of confinement $\zeta$ and flow rate $Q$ increase and decrease, respectively (Fig. 5). These trends are consistent with those observed in experiment. Near-quantitative agreement between simulation and experiment is observed when the nanopost spacing is relatively small (i.e. $\zeta \leq 0.25$) or large ($\zeta \geq 0.4$) at the lowest flow rates. Generally, though, simulation systematically slightly over-predicts $V_x$. The flow rate used in the simulation is calculated from the bulk flow rate imposed at the inlet of the microchannel in the experiments in Ref. [28] and likely represents an overestimate of the flow field within the closely-spaced nanopost arrays. The largest discrepancies between simulation and experiment occur at intermediate values of the confinement parameter $\zeta \approx 0.3$ for all flow rates. This behavior is expected because attractive particle-post interactions, which have been neglected in simulation, will most strongly influence particle transport in the size regime where the particles experience the greatest heterogeneity in their local environment. Nevertheless, the values of $V_x$ from simulation and experiment are within a factor of 2 for all conditions examined, which is remarkable considering the fundamental physical assumptions made in formulating the minimal computational model.

Next, we use simulation to quantify the extent of particle dispersion through the nanopost
arrays. Specifically, we compute the dispersion coefficients

\[ D_{L,T}(t) \equiv \frac{1}{2} \frac{d\sigma_{L,T}^2(t)}{dt}, \]  

(4)

which are defined in terms of the second moments of the particle displacements \( \sigma_{L,T}^2(t) \) in the longitudinal (L) or transverse (T) direction, respectively [56]. With this definition, coefficients from the classical advection-dispersion equation are recovered when \( \frac{d\sigma_{L,T}^2}{dt} \) is constant. The coefficients \( D_{L,T} \) can be calculated directly from particle velocity auto-correlation functions [56] or the long-time behavior of the particle mean-square displacements (MSDs), determined in the frame of reference of the average velocity of all the particles, \( \bar{V}_x \) [41]. Here, we calculate the longitudinal particle MSDs in a co-moving frame, \( \sigma_L(t) = \langle (x(t) - \bar{V}_x t)^2 \rangle \), and then use Eqn. 4 to obtain \( D_L(t) \) and \( D_T(t) \). This procedure differs from that used in Ref. [28], which employed a scaling relationship to estimate the asymptotic dispersion coefficients. To facilitate direct comparison with simulation, we calculate \( D_L(t) \) and \( D_T(t) \) for the experimental data from that study using Eqn. 4. In performing the analysis, we observed that the time-dependent dispersion coefficients \( D_L(t) \) and \( D_T(t) \) from experiment are approximately constant at short lag times \( t \) but increase at longer times, reaching an asymptotic plateau in some cases but not in others. The behavior is due to the fact that individual particles can only be tracked for finite times in experiment before they move out of the field of view; in some cases this time is not long enough probe the limiting behavior of \( D_L(t) \) and \( D_T(t) \). To compare with simulation across the different post spacings and flow rates, we define a dimensionless time scale \( \tau = t\bar{V}_x / S \) and calculate \( D_L(\tau = 1) \) and \( D_T(\tau = 1) \), which captures the extent of dispersion over the time needed to transit a single pore. Qualitatively similar results were found using other values of \( \tau \).

The normalized longitudinal dispersion \( D_L/D_q \) in the simulations is approximately 1 at the lowest \( \text{Pe}_x \approx 0.5 \), and increases concomitantly with \( \text{Pe}_x \) (Fig. 6(a)). For \( \text{Pe}_x \geq 2 \), the data from experiment and simulation are in excellent agreement. At lower values of \( \text{Pe}_x \), however, the values of \( D_L/D_q \) from experiment are less than one and lie somewhat below the simulation data, differing by a factor of \( \leq 2 \). This discrepancy suggests that weak attractive interactions between the particles and the nanoposts affect particle dispersion in this regime. Indeed, similar discrepancies are also observed when comparing the normalized \( D_T/D_q \) values. The values of \( D_T/D_q \) obtained from simulations in which nanoparticle-post attractions are neglected are nearly independent of \( \text{Pe}_x \) over the studied range, with
$D_T/D_q \approx 1$. By contrast, the $D_T/D_q$ values calculated from the experimental trajectories are less than unity, in accord with the narrower transverse velocity distributions observed in the experiments (cf. Fig. 4), and increase as a weak power-law with $Pe_x$. Hence the weak attractions between the nanoparticles and posts in experiment depress transverse dispersion across the entire range of $Pe_x$ but depress longitudinal dispersion only for $Pe_x \leq 1$ (i.e. when particles advect more slowly than they diffuse). Together, these results suggests the minimal LPT model is able to most accurately describe dispersion behavior in the advection-dominated regime, where particle transport is relatively insensitive to the nature of the particle-post interactions.

FIG. 6. (a) Normalized longitudinal and (b) transverse dispersion coefficients as a function of the Péclet number $Pe$ for the flow rates indicated in the figure legend. Closed symbols: simulations; open symbols: experiments, calculated from the data of Ref. [28].
IV. CONCLUSIONS

We have presented a minimal computational model that semi-quantitatively reproduces the transport properties of particles strongly confined in a quasi-2D nanopost array [28]. In our modeling approach, the flow field within nanopost arrays is calculated using the Lattice Boltzmann method. Subsequently, Lagragian particle tracking is used to obtain trajectories of finite-sized particles in the Lattice Boltzmann flow field. Distributions of particle velocities along the direction of flow are asymmetric when the nanoposts are closely spaced, reflecting contributions from caging and from advection. The velocity distributions obtained in the experiments of Ref. [28] are similarly bimodal when the dimensionless confinement parameter $\zeta$ is large. The distributions of particle velocities normal to flow in simulation are non-Gaussian, as in the experiments of Ref. [28], but narrow more slowly when $\zeta$ is increased. The average longitudinal velocities obtained in simulation and experiment are in semi-quantitative agreement. Longitudinal dispersion coefficients from simulation and from experiment are in near-quantitative agreement at high Pe but diverge at low Pe; the transverse dispersion coefficients obtained from simulation, however, are slightly larger than those obtained in experiment.

The good agreement for metrics characterizing transport along the flow direction between the minimal computational model and the experimental data of Ref. [28] suggests that viscous drag on particles from the fluid flow field dominates the longitudinal transport. It also indicates that the coarse level of treatment of hydrodynamic interactions in the LPT method, which neglects fluctuations in fluid velocity field and momentum transfer from the particle to the fluid, is sufficient to model flow-driven nanoparticle transport through nanopost arrays. Surprisingly, comparison with experiment suggests that the principal shortcoming of the model is the treatment of the nanoparticle-post interactions. The elastic collision model used in the LPT simulations neglects weakly attractive nanoparticle-post interactions that influence particle transport in the longitudinal direction when Pe $< 1$ and transverse particle dispersion. Although these interactions have not been characterized in the experimental systems, they are assumed to be short-range ($\ll d_{np}$) van der Waals or screened electrostatic interactions. Implementing such interactions in the model is straightforward, but it requires using a significantly smaller time step (ca. 5 order of magnitude smaller) to integrate the particle equations of motion, which greatly diminishes the computationally efficiency of the
LPT method in simulating long-time transport behavior. We posit that this challenge can be addressed in future studies by combining the LPT method with event-driven molecular dynamics or kinetic Monte Carlo like algorithms to simulate transient particle adsorption on the nanoposts. Validating these modeling approaches, however, will require comparison with new experimental systems in which the nanoparticle-post interactions have been thoroughly characterized.

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