

Nanoparticle transport models in confined fluids

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ABSTRACT

Nanoparticle (NP) transport in confined fluidic structures has applications in areas of energy, nano manufacturing and biomedical industries. NP diffusion under nanoscale confinement was studied using mesoscale particle dynamics with interactions determined by colloidal physics. We find that at this scale, subtle changes in the geometry of confinement produces changes in energy barrier that results in changes of diffusion transport mechanism and NP penetration into nanoconfined structures. The results were correlated with continuum methods to determine effective diffusivities of fluids that accommodate the NP interactions. Our models will contribute towards better understanding of phenomena for optimizing NP transport in drug delivery systems and other nanoscale devices.

Keywords: nanoparticle, boundary, diffusion, interface, transport

1 INTRODUCTION

Transport phenomena involving colloidal NP suspensions in complex environments are important in several biomedical [1,2] and engineering applications [3, 4]. Most approaches for studying such transport treat the suspension as a continuum. While continuum methods are well researched for studying transport behavior and fluid mechanics in a vast array of applications [5], they do not consider the particle interactions. However, when the size of the complex nanoscale confining environments approaches that of the NPs, the interactions amongst NPs and between NPs and the environment needs to be taken into account. Specific examples of such systems are encountered in NP transport through nanochannels used in drug delivery and nanofluidic cooling systems [6-8]. In such ionic colloidal suspensions the NPs acquire characteristic surface charges which results in a surface potential and a double layer of co- and counter-ions from the solution. According to DLVO theory, this double layer

results in an interaction energy among the nanoparticles as [9]:

$$W(r) = \frac{64\pi k_B T R \rho_\infty \gamma^2}{\kappa^2} \exp(-\kappa r) \quad (1)$$

where r is the separation between NP surfaces, and R is the radius of the NP, ρ_∞ is the concentration of ions in the suspension, κ^{-1} is the Debye screening length (characteristic size of the double layer) and k_B and T are the Boltzmann constant and the temperature. When κ^{-1} approaches the size range of the particles, the interactions amongst the particles may span several times the particle size and play an important role in the diffusion of the particles.

Typical experimental and theoretical methods used to investigate NP diffusion in such systems address classical diffusion of such particles in bulk or at the atomistic scales [10-16]. Molecular Dynamics (MD) simulations are useful to model NP interactions in a solution at the atomistic level [17, 18] but limit possibilities to study nanoscale systems over long time periods. Coarse grained, mesoscale MD of NP systems can implicitly account for solvent effects and can be used to study NP transport under confinement. [19, 20].

Here we study NP transport kinetics and concentration profiles and discusses the role of geometry and material properties in the modulation of energy barriers for diffusion. We also correlate these results to continuum based methods for determining effective diffusion coefficients of NPs under confinement.

2 METHODS

Figure 1 shows a schematic of the system we used to study the transport of 20nm NPs from a reservoir into a confining nano channel. NPs had a density of about 2.2g/cc and their concentration was set at 10^{19} per liter. The minimum NP separation of about 22nm is much larger than

the Bjerrum length and thus justifies the mean field approximation of the solvent[24]. The nanochannel walls were embedded with “site” particles in a triangular tiled pattern with a 20nm separation and periodic boundary condition was applied in y and z directions.

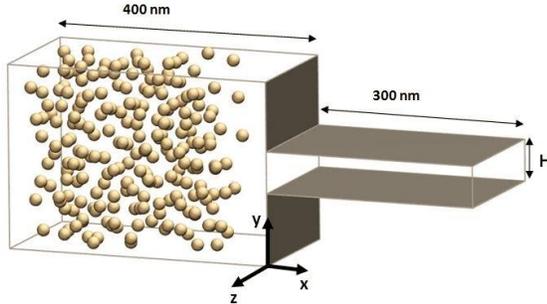


Figure 1 : System setup showing arrangement of NPs in reservoir before transport simulation.

Interactions between NPs were modeled with the hard core repulsive Yukawa potential which conforms with equation (1) and NP –wall interaction was modeled with an attractive Morse-stretch potential both with a cut-off of 10nm. Trajectories of the NPs were obtained through simulations using LAMMPS [25, 26] and ensemble averages of 5 replicas were used for further analysis.

Subsequently, discretised continuum diffusion finite element method [2, 27] that accounts for NP adsorption was adapted to match results from the particle trajectories and obtain effective diffusion coefficients.

3 RESULTS AND DISCUSSION

The average fraction of NPs accumulating in the channel was used to study the kinetics of NP transport. Figure 2 shows the accumulated fraction for various conditions. Initially, the particles attach interact with the sites on the wall without any hindrance during the ballistic regime. This lasts for about 0.006 ms and the rates of accumulation vary only by about 20% under all conditions. Once a monolayer of particles are attached to the channel wall, the diffusing NPs start interacting with the adsorbed NPs and this results in the long time diffusive regime. During this regime the diffusion of particles is heavily modulated by variations in material properties and size of the channel. When the channel height is 90nm, the accumulation saturates exponentially indicating a first order reaction rate. However, with a reduction in the channel height by 1.5x the particle size to 60 nm, a linear accumulation curve is obtained that resembles a zero order reaction rate.

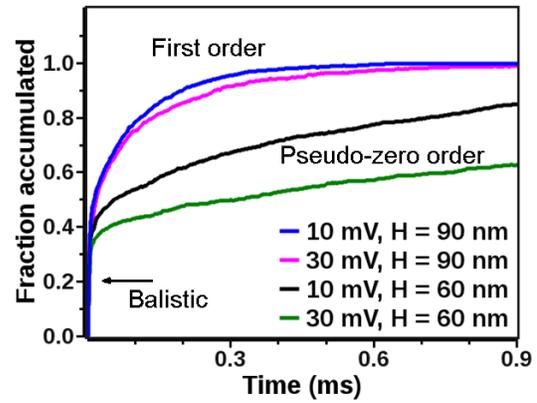


Figure 2. Nanoparticle accumulation in nanopores for different nanopore size and nanoparticle surface potential. The ballistic regime is very short and the differences in the nature of accumulation curves for different conditions indicate changes in mechanisms of transport.

This drastic change in the mechanism of reaction is due to the repulsive energy barrier presented by the adsorbed particles at the entrance of the nanochannel. Since the inter-NP potential is completely repulsive, the adsorbed particles reduce the available space for further NPs to enter the nanochannel. The formation of such a barrier becomes even more evident when the surface potential intensity is increased to 30 mV - increase in surface potential results in a higher repulsion among particles and hence a lower rate and linear accumulation curve at 60nm. In both the cases, the 90 nm channel is still sufficiently high and provides enough space for NPs to enter the channel although the accumulation is un-hindered as in the ballistic regime.

The exact nature of the energy barrier is demonstrated in figure 3 that shows the average potential energy of a particle along the length of the system. Clearly, the size of plays a major role in determining the extent of the energy barrier, which is a consequence of the exponential decay of the inter-NP interaction of equation (1). First order kinetics imply a time dependence of accumulated fraction according to:

$$f_p(t) = f_{r0}(1 - \exp(-k \cdot t)) \quad (2)$$

where $f_c(t)$ is the fraction of particles in the channel at time t , f_{r0} is the initial fraction of particles in the reservoir at the start of the process and “k” is the rate constant of the reaction. Equation 2 fits well into the saturation behavior seen in the 90 nm channels of figure 2. The ΔE indicated in figure 3 is the effective energy barrier associated with the kinetics of the reaction according to Arrhenius relationship. An increase of six orders of magnitude in ΔE , results in a

drastic reduction in the k , such that equation (2) approaches a straight line as observed in the 60 nm accumulation curves of figure 2.

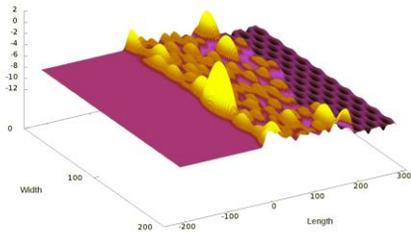
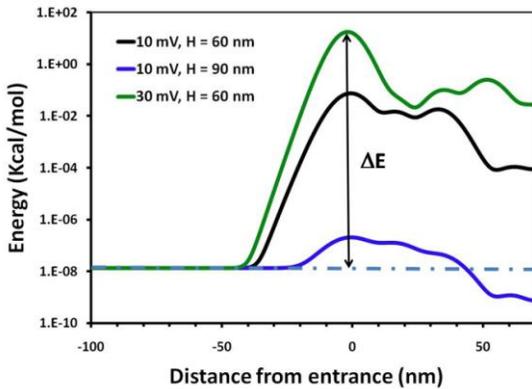


Figure 3: (top) Average potential energy of a single representative particle as a function of the length of the system. The colors correspond to 3 of the different conditions presented in fig 2. A slight change in the channel width has resulted in a change in energy barrier at the entrance by six orders of magnitude (bottom) a 3D view of the potential energy surface for the system with 10 mV and $H = 60$ nm

To bridge nanoscale discrete and macroscopic continuum levels we explored NP diffusion for various H using recently developed FE method [2]. Effective diffusivities D_E were calculated by adjusting linear diffusivity dependence on NP concentration and NP adsorption on nanochannel surface in order to match cumulative NP accumulation in diffusive regime by colloidal model of Figure 2. D_E is plotted in Figure 4 as a function of channel height.

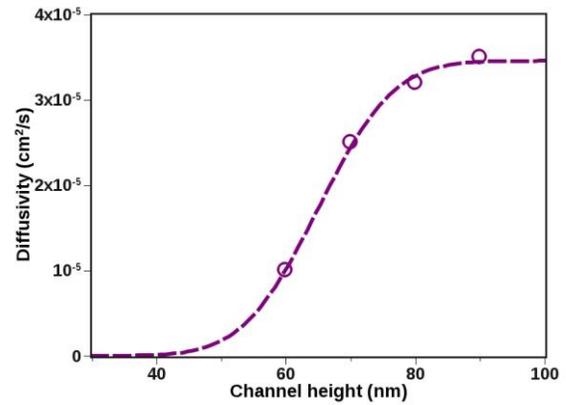


Figure 4: Effective diffusivity as a function of channel height indicates a drastic reduction in diffusion with subtle changes in channel size.

4 CONCLUDING REMARKS

Our analysis suggests that “top-down” approach alone in nanoscale structures could omit important microscopic processes, but the combination of continuum and particle methods may turn out to be useful approach in nanofluidic structure design by accommodating nanoscale effects.

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