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Understanding adsorption behavior of silica nanoparticles over a cellulose surface in an aqueous medium

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HIGHLIGHTS

- BD study delineates the mechanism of suspension and adsorption of nanoparticles.
- The electrostatic screening length controls particles' suspension and adsorption.
- Adsorbed particles form a monolayer, independent of their bulk concentration.
- The monolayer is either gas or liquid like, depending on their bulk concentration.

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ABSTRACT

The suspension and adsorption of silica nanoparticles on a cellulose surface, in an aqueous medium is investigated using Brownian dynamic simulations. The inter particle and particle–surface interactions are modeled within the framework of the DLVO theory. Our analysis predicts the accumulation of negatively charged nanoparticles near a negatively charged surface depending on the Debye screening length of the medium. A crossover from the suspension to the adsorption of negatively charged silica nanoparticles onto a negatively charged cellulose surface has been reported as the screening length (k^{-1}) of the medium increases. The crossover is observed at $k^{-1} = 100$ nm, due to the interplay between the nanoparticle–nanoparticle and the nanoparticle–surface interactions. The adsorption behavior of nanoparticles is explained using the potential of mean force analysis. The amount of nanoparticles adsorbed depends on their bulk volume fraction (ϕ) and the screening length of the medium. Further, the effects of electrical potentials of nanoparticle (Ψ_P) and surface (Ψ_S) on the adsorption are reported. The data suggests that the adsorption of nanoparticles increases either with increasing Ψ_P magnitude, or/and, with decreasing Ψ_S magnitude. The adsorbed particles form a disordered monolayer, and undergo subdiffusive motion. We have also observed a transition from the gas-like structure to the liquid-like structure of nanoparticles in the adsorbed monolayer as their bulk volume fraction increases.

1. Introduction

Adsorption of nanoparticles and their self-assembly on surfaces are common to many fields of engineering such as film manufacturing, coating, and catalysts (Johnson and Lenhoff, 1996; Kasemo et al., 2000; Nakanishi et al., 2001; Nepal et al., 2012; Zhang and Bai, 2002). Self-assembled and ordered structures of adsorbed nanoparticles on a surface are fascinating owing to their unique optical and electronic properties. For example, silica nanoparticles adsorbed on a modified glass substrate finds application in antireflective coatings (Hattori, 2001; Liu and Yeh, 2010). In addition, coatings of various different particles on substrates are used in data storage, sensors (Chaikin et al., 2013; Velev and Kaler, 1999), lithography masks (Hanarp et al., 2003), and template for photonic crystals (Joannopoulos et al., 1995). Adsorption of biomolecules like protein on surfaces are also very useful for biomaterial selection (Jeon et al., 1991), medicines and enzyme-enhanced laundry detergents. The collective properties of adsorbed nanoparticles on a surface are largely dependent on their arrangement. Therefore, in many engineering applications, heterogeneous surfaces are used to control the structure and dynamics of adsorbed particles (Adamczyk et al., 2002, 2005). It is also shown that surfaces pre-covered with smaller particles are very promising candidate for membrane filtration and anti-biofouling (Adamczyk et al., 2001). Similarly, patterned surfaces with grooves or holes are fabricated to generate a large area defect free ordered array of particles

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Nomenclature

A_{pp}	Hamaker constant for the interactions between a pair of nanoparticles, J
A_{ps}	Hamaker constant for the interactions between nanoparticle and surface, J
$A_{Surface}$	Area of a single surface, dimensionless
a	Radius of a nanoparticle, nm
$\overline{a}$	Radius of a nanoparticle, dimensionless
B_{PP}	Yukawa coefficient for particle–particle interaction, dimensionless
B_{PS}	Yukawa coefficient for particle–surface interaction, dimensionless
e	Electronic charge, C
$\overline{F}_C$	Conservative force, dimensionless
$\overline{F}_f$	Frictional drag force, dimensionless
$\overline{F}_r$	Random force, dimensionless
F_f	Frictional drag force, kg m/s^2
F_r	Random force, kg m/s^2
F_{PP}	Force between two nanoparticles, dimensionless
F_{PS}	Force between nanoparticle and surface, dimensionless
$g_{in\text{-}plane}(r)$	2D-radial distribution function, dimensionless
$g_{bulk}(r)$	Radial distribution function of all the particles in the system, dimensionless
h_p	Peak height of a z-density profile, dimensionless
k_B	The Boltzmann constant, J/K
k^{-1}	Screening length, nm
ka	Inverse of screening length, dimensionless
L_X	Simulation box length in x-direction, dimensionless
L_Y	Simulation box length in y-direction, dimensionless
$\overline{m}$	Mass of a nanoparticle, dimensionless
m	Mass of a nanoparticle, kg
MSD	Mean squared displacement, dimensionless
$n(z)$	Number of nanoparticles within a distance between z and $z+\Delta z$ along z direction
N_{box}	Total number of particles in the box
$n_{ad}(\bar{t})$	Number of nanoparticles adsorbed on the surface at time $\bar{t}$
N_{ad}	Total number of nanoparticles adsorbed on the surface
N_m	Total number of nanoparticles in a monolayer
$\langle N(r, r+\Delta r)\rangle$	Average number of particles in a circular bin between two distances r and $r+\Delta r$ from the center of a particle
$\langle N_b(r, r+\Delta r)\rangle$	Average number of particles in a spherical bin between two distances r and $r+\Delta r$ from the center of a particle
PMF_{PP}	Potential of mean force between two particles, dimensionless
PMF_{PS}	Potential of mean force between particle and surface, dimensionless
r	Center to center distance between two particle, dimensionless
$r_i(\bar{t})$	Position vector of a nanoparticle 'i' at a time,$\bar{t}$
Δr	Bin width for $g_{bulk}(r)$ and $g_{in\text{-}plane}(r)$, dimensionless
T	Temperature, K
$\overline{T}$	Temperature, dimensionless
$\bar{t}$	Time, dimensionless
t	Time, s
Δt	Time step, ns
U	Interaction energy, dimensionless
U_{PP}	Interparticle interaction energy, dimensionless
U_{PS}	Particle–surface interaction energy, dimensionless
$U_{EL(PP)}$	Electrostatic interaction energy between two particles, dimensionless
$U_{EL(PS)}$	Electrostatic interaction energy between a particle and the surface, dimensionless
$U^{att}_{LJ(PP)}$	The effective Lennard-Jones attractive interaction energy between two particles, dimensionless
$U^{att}_{LJ(PS)}$	The effective Lennard-Jones attractive interaction energy between particle and surface, dimensionless
$U^{rep}_{LJ(PP)}$	The effective Lennard-Jones repulsive interaction energy between two particles, dimensionless
$U^{rep}_{LJ(PS)}$	The effective Lennard-Jones repulsive interaction energy between particle and surface, dimensionless
V_{box}	Volume of the simulation box, dimensionless
v	Velocity of a particle, m/s
$\overline{v}$	Velocity of a particle, dimensionless
z	Distance between the center of a particle and the surface, dimensionless
Δz	Bin width for ρ_z, dimensionless
Ψ_s	Electrical potential of the surface, mV
Ψ_p	Electrical potential of the nanoparticle, mV
$\overline{\Psi}_S$	Electrical potential of the surface, dimensionless
$\overline{\Psi}_P$	Electrical potentials of the nanoparticle, dimensionless
η	Viscosity of solvent, Pa s
$\theta(\bar{t})$	Surface coverage, dimensionless
θ_{max}	Maximum surface coverage, dimensionless
θ_∞	Surface coverage in infinite time, dimensionless
ε	Dielectric constant of the solution, dimensionless
ε_0	Dielectric permittivity of free space, F/m
ϕ	Bulk volume fraction of nanoparticles, dimensionless
Γ	Damping factor of the medium, s
ρ_z	z-density of nanoparticles, dimensionless
τ_0	Time, ns
σ	Exclusion thickness, dimensionless

over surfaces (Juillerat et al., 2005). Moreover, square shape charged stripes on a surface induce a great degree of order among the adsorbed particles on it (Brewer et al., 2010). In addition to the adsorption of particles and their arrangement over a surface, the suspension of particles in an aqueous medium is also important for many nano-biotechnological applications. For example, proteins, which are present in blood or solution, get adsorbed on an artificial surface to which they are exposed. Hence, minimizing protein adsorption, is important in areas of blood-contacting devices, chromatographic supports, contact lenses, immunoassays, etc. (Jeon and Andrade, 1991; Jeon et al., 1991). Therefore, the behavior of nanoparticles, proteins, viruses and various other macromolecules on surfaces have received considerable research interests in recent years.

Various models have been proposed to properly capture the adsorption of particles over surfaces in last few decades. The earliest one is the random sequential adsorption model (RSA) (Feder, 1980). In this model, particles are individually and randomly placed on a surface such that no particle overlaps with previously placed particles. At a time one particle is placed on the surface, and it remains permanently fixed to its adsorbed position. However, this model does not incorporate some important aspects of the process – such as explicit particle–surface interactions,