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Reversible adsorption kinetics of near surface dimer colloids

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Abstract

We investigate the effect of shape on reversible adsorption kinetics using colloidal polystyrene dimers near a solid glass surface as a model system. The interaction between colloid and wall is tuned using electrostatic, depletion, and gravity forces to produce a double well potential. The dwell times in each of the potential wells is measured from long duration particle trajectories. The height of each monomer relative to the glass surface is measured to a resolution of <20 nm by in-line holographic microscopy. The measured transition probability distributions are used in kinetic equations to describe the flux of particles to and from the surface. The dimers are compared to independent isolated monomers to determine the effects of shape on adsorption equilibria and kinetics. To elucidate these differences, we consider both mass and surface coverage and two definitions of surface coverage. The results show that dimers with single coverage produce slower adsorption and lower surface coverage in comparison to monomers while dimers with double coverage adsorb faster and result in higher surface coverage.

Introduction

Transport kinetics of large molecules, such as proteins, near interfaces depends on many factors including their size, charge, shape, and deformability. Current modeling approaches often treat proteins as colloidal particles in order to capture effects arising from their size and shape.^{1–3} These models are used to describe the adsorption of proteins on solid surfaces and fluid-fluid interfaces.^{4–6} Adsorption experiments involving biomolecules, such as proteins, involve many complicating factors including pH, ionic strength, and protein quality. This makes direct comparisons with theoretical models challenging.^{7,8} The results of detailed experiments have yielded subpopulations of molecules that exhibit different kinetics, the mechanisms of which are not well understood.⁹

The dynamics of individual molecules have been shown to play an important role in transport kinetics, even at dilute concentrations. For instance, single molecule tracking experiments have given more detailed insights into the kinetics of proteins at interfaces.¹⁰ Individual particle tracking has shown that protein-protein interactions and protein conformation can change the residence time of proteins on the interfaces and enhance clustering on the interface.^{11,12} The effect of particle shape supports previous studies that fit protein surface coverage experiments to kinetic models of non-spherical molecules.⁴ In

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particular, the overshoot in surface coverage as a function of time was fit to models based on roll over from an end-on adsorbed state to side-on adsorbed state.

Colloid models have been useful guides for developing understanding of protein adsorption.^{1,13} Experimental studies have shown that deposition of colloids can be useful models for irreversible adsorption, validating random sequential adsorption models¹⁴ and diffusion-kinetic models.^{15–17} The advantage of using colloids as a model system is the possibility to more carefully control experimental parameters and track particles directly, thereby gaining insight into the underlying mechanisms for adsorption. The challenge with using colloids as a model system is the system must be tuned to produce behaviors comparable to the system of interest.

Previously we have shown that colloids can be used to study reversible adsorption kinetics through measurements of individual particle trajectories.¹⁸ In this paper, we explore the effect of shape on transport kinetics through the use of dimer colloids. The dimers are composed of two colloidal spheres irreversibly bonded together, allowing for two adsorption sites to the surface. We investigate the kinetic transitions between side-on and end-on orientations of individual particles to better understand how nonspherical shape effects these kinetics.

The interaction between colloids and a planar glass surface is tuned using a combination of electrostatic, gravitational, and depletion forces to produce a double well interaction potential. The near surface potential well is defined as an adsorbed state, while the outer well is defined as a desorbed state. The interaction potential is tuned to allow for a large number of transitions between adsorbed and desorbed states to be observed from following a single particle.

We measure the height of a colloidal particle relative to the interface using in-line holographic microscopy.^{19–21} For a better comparison between monomers and dimers, we track the state (adsorbed or desorbed, denoted A or D) of each sphere. The dimer can be in one of three states, both sides adsorbed (AA), one side adsorbed and the other desorbed (AD), and both sides desorbed (DD). The transitions between these three states are affected by the position and orientation of the dimer relative to the wall through hydrodynamic and conservative forces. How these forces affect the kinetics is captured by measuring the survival times within each state. The transition probabilities between states are used in kinetic equations that describe the reversible ideal adsorption as a function of initial particle concentration. In this way, the reversible adsorption kinetics of dimer colloids can be compared directly with that of isolated monomer colloids, therefore demonstrating the effect of particle shape.

We first introduce our experimental setup and methods for image processing. Next we present the probability distributions for transitions between the different adsorbed states. The measurement of interaction potential for the dimers and monomers are then compared to show the effect that dimer shape has on the interaction energy. The measured probability distributions for transitions between states are presented and discussed for both monomers

and dimers. Finally, the ideal adsorption kinetics are modeled using kinetic equations with fluxes determined from the measured probability distributions.

Materials and methods

Imaging

Images are generated using in-line digital holographic microscopy and analyzed using Hology software developed by the Manoharan research group for tracking colloidal clusters.^{19,20,22} A sample cell constructed from double-sided tape is observed with an Olympus IX71a inverted microscope using a 60 $\times$ water (1.2NA) objective. The sample is illuminated with a collimated beam from a 4 mW 635 nm laser diode source (Thorlabs LDM635) mounted in the microscopy lamphouse. Images are recorded using an Andor Zyla 5.5 sCMOS camera at 20 frames per second with 3 $\times$ 3 binning. The background image used to normalize the images is produced with a median filter over the time-sequence, which serves to remove all stationary features.

The images are fit to reference images generated from scattering theory using the “LMFIT” software package.²³ The scattering pattern from monomers is analyzed using the Mie scattering theory while the T-matrix method, which accounts for the coupled scattering from multiple particles, is used for dimers.^{19,24–26} The fitting procedure begins with an appropriate position and a cropped portion of the image centered on the particle. The initial position in the first frame is guessed manually while the fitting position is used as an initial guess in the next frame's fitting. For fitting the dimer position, the center-to-center distance of the two particles is fixed at two particle radii and the dimer centroid, azimuthal angle, and polar angle are fit. We then extract the Cartesian positions for each sphere in the dimer for analysis.

Sample Preparation

We prepare dimers by adding 100 mmol/L salt to a solution of individual particles (polystyrene spheres with $a=1$ μm radius), which reduces electrostatic screening between the spheres and allows them to aggregate.²⁷ This solution is held quiescently for 5 min until the resulting aggregates are repeatedly washed with millipore water and centrifugation to return the aggregates to a low salt concentrations and inhibit further aggregation. The majority of spheres remain isolated and approximately 5 % are clusters of 2 or greater.

The particle solution is diluted such that only 1 to 3 monomers or clusters are observed in a single image frame and do not interact with neighboring particles. Only monomers and dimers are tracked for this study.

A chamber is built by cutting a 1 cm² rectangular hole in piece of 500 μm thick teflon tape. The Teflon tape is attached to a microscope slide and the hole is filled with the sample solution. A 25 mm coverslip is placed over the teflon tape and sealed along the edges

^aCertain commercial materials and equipment are identified in this paper in order to adequately specify the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that these are necessarily the best available for the purpose.

using epoxy. The chamber is placed on the microscope stage for at least an hour to allow the system to equilibrate before measurements are made. Small drift in the particle height of about 10 nm over the duration of an observation was subtracted using the position in the adsorbed state as a reference height.

The particles are dispersed into a sample solution consisting of 1 mmol/L Sodium Chloride (NaCl) and 0.8 Vol % charged colloidal silica (Ludox TMA radius $(13.4 \pm 1) \text{ nm}^{28}$). The charged colloidal silica acts as a depletant via electrostatic force.²⁹ The combination of gravitational, electrostatic, and depletion forces create a double well potential.

Theory

The double well interaction potential between a sphere and the bottom microscope slide is produced by a sum of depletion, electrostatic, and gravitational potentials,

$$U_{tot} = U_{dep} + U_{el} + U_g. \quad (1)$$

The interaction potential between the sphere and the glass surface produced by a charged depletant is calculated using a force balance approach developed by Sharma and Walz.^{30,31} The depletion length scale is small ($\approx 100 \text{ nm}$) compared to the sphere radius ($1 \mu\text{m}$); we assume that the potential between each sphere in the dimer and the glass wall is unperturbed by the adjoining particle. The electrostatic interaction energy between sphere and wall is³²

$$U_{el}(h) = 4\pi\epsilon_r\epsilon_0(k_bT/e)^2 aY_1Y_2 \exp(-\kappa^*h), \quad (2)$$

where h is the distance between surfaces, a is the sphere radius, ϵ_r is relative permittivity of the medium, ϵ_0 is the vacuum permittivity, e is the elementary charge, Y_1 and Y_2 are the effective surface charges of the sphere and wall respectively. κ^* is an adjusted inverse Debye length introduced due to the enhanced screening caused by the charged silica.²⁹ The gravitational potential energy is given by

$$U_g = \frac{4}{3}\pi a^3 (\rho_p - \rho_b) gh, \quad (3)$$

where g is gravitational acceleration, ρ_p is the density of the polystyrene spheres ($\rho_p = 1.05 \text{ g/cm}^3$), and ρ_b is the bulk solution density, which when adjusted for the addition of colloidal silica is $\rho_b = 1.009 \text{ g/cm}^3$.

Transition rates

We use this double well interaction potential to define two domains where a monomer sphere is considered either adsorbed (A) and desorbed (D). The barrier between the potential wells is used as a boundary between these two domains. The trajectory of the particle as it diffuses within the potential well is analyzed in order to determine the distribution of dwell times within each of these two domains. Previously, we demonstrated that these dwell times

depend on the shape of the interaction potential and the height dependent diffusion coefficient of the particle.¹⁸

In the case of dimers, we track the position of each sphere of the dimer to determine a whether the particle is in one of three states: both adsorbed (AA), one adsorbed and one desorbed (AD), and both desorbed (DD).

If the barrier crossing timescale is dominant, the probability of crossing the barrier can be described by the Kramers' dwell time distribution and transitions will be exponentially distributed. The characteristic timescale is the characteristic Kramers' dwell time, τ_K .³³ The probability density function for the particle to cross from adsorbed (A) to desorbed (D) is

$p_{A \rightarrow D}(t) = \frac{1}{\tau_K} e^{-t/\tau_K}$. In contrast, the crossing from a shallow potential does not satisfy the conditions for Kramers' approach due to the long diffusive timescale within the shallow well.¹⁸ We use the solution of 1-D diffusion in a linear (gravitational) potential with a reactive boundary condition to describe the probability of escape, $p_{D \rightarrow A}(t)$.³⁴ In experiments, we measure the dwell times in each domain and compare the results to cumulative escape probability, $T(t) = \int_0^t p(\tau) d\tau$.

The same approach is used to analyze the kinetics of dimer particles. The state of each sphere in the dimer is determined as a function of time. As noted above, the dimer system can be in one of three states: AA, AD, or DD. We assume that only one sphere in the dimer can transition at a given time, i.e., there are no transitions directly between the AA and DD states. This leaves four transitions: two where a sphere desorbs, $AA \rightarrow AD$ and $AD \rightarrow DD$, and two where a sphere adsorbs, $DD \rightarrow AD$ and $AD \rightarrow AA$.

In comparison with the kinetics of monomers, the anisotropic shape of the dimers makes prediction of the escape probability distributions difficult. For instance, the desorbed particle in the AD state will be confined to a region closer to the interface than if it were free to diffuse. The anisotropic diffusion of the dimer near the surface also introduces hydrodynamic resistance that is sensitive to the particle orientation. Therefore we do not make predictions about escape probability distributions, but rather use the measured distributions to predict how a population of particles will adsorb to the surface. We discuss how the measured probability distributions are used in coupled transport equations in the following section.

Adsorption Kinetics

The concentration of particles in a given state i is denoted by c_i , which are normalized by the close-packed concentration spheres in a monolayer. For monomers, there are two states A and D and the total concentration is fixed, $c_T = c_A + c_D + c_0$, where c_0 is the particles in an initial state.

We seek to model the evolution of adsorption (c_A) to an initially uncovered surface, using experimentally determined transition probability distributions. Since these distributions are obtained from the dynamics of isolated particles, our resulting predictions are ideal and assume no interactions among particles. The transition probability distributions, $p(t)$, give

the flux of particles to a new state as a function of time. Particles that arrive in a new state will leave that state as a function of dwell time, $t-t'$, where t' is the time of entry into a new state. The concentration of particles that enter a new state at a given time, t' , over a time step, Δt , are stored as $c_A(t') = c_A(t') - c_A(t' - \Delta t)$. The concentration of particles that enter the new state will decay with the escape probability set by $p(t-t')$. This approach allows us to use experimentally measured probability distributions without assuming a function form for the distributions.³⁵

We introduce particles to the desorbed state using a probability distribution (i.e., decaying c_0), that describes the settling of particles towards the surface from an initial position in the linear potential.³⁴ The initial position of population c_0 is set here by the average height of monomers in the linear gravitational potential, $h_0 = 1.6 \mu\text{m}$. This height is chosen in order to avoid kinetics that are sensitive to the initial condition, which may arise if h_0 is set at a height close to the surface. Similarly, a large value for h_0 would introduce large differences in sedimentation to the surface between monomers and dimers. The timescale where half of the c_0 population transitions to the desorbed state is 7.6 s for both monomers and dimers when $h_0 = 1.6 \mu\text{m}$.

The balance of fluxes between states A and D based on the experimentally derived probability distributions is determined by discrete kinetic equations for the concentration of each state:

$$\begin{aligned} \frac{\Delta c_A(t)}{\Delta t} &= B(t) \sum_{t'} \Delta c_D(t') p_{D \rightarrow A}(t-t') - \sum_{t'} \Delta c_A(t') p_{A \rightarrow D}(t-t'), \\ \frac{\Delta c_D(t)}{\Delta t} &= \sum_{t'} \Delta c_A(t') p_{A \rightarrow D}(t-t') - B(t) \sum_{t'} \Delta c_D(t') p_{D \rightarrow A}(t-t') + c_0(t) p_{0 \rightarrow D}(t). \end{aligned} \quad (4)$$

The adsorption flux is modified by the concentration of open sites, $B(t) = 1 - c_A(t)$. This term acts to block particles that would have adsorbed if there were open sites.

This same approach is extended to the dimer system for transitions between AA , AD , and DD states. We use two kinetic equations for the concentrations of c_{AA} and c_{AD} and the concentration of DD particles is subject to the fixed particle constraint $c_T = 2c_{AA} + 2c_{AD} + 2c_{DD} + 2c_0$. The dimer system includes two adsorbing transitions, DD to AD and AD to AA , both of which are modified by the concentration of open sites. We compare two situations for how a dimer will block surface sites. First we consider contribution to surface blocking only from adsorbed particles; the concentration of open surface sites defines the blocking function, $B_1(t) = 1 - 2c_{AA} - c_{AD}$. This model is denoted B1. The other case assumes that a dimer will occupy two surface sites regardless of how many particles are adsorbed, this gives a blocking function, $B_2(t) = 1 - 2c_{AA} - 2c_{AD}$ and is denoted B2. As with the monomers, the particles that are blocked from adsorption are kept in the same state. The dimers are introduced to the system from c_0 in the same way as monomers. The probability distribution that describes dimer settling to the interface is modified by doubling the gravitational force of a monomer and includes the orientation-averaged translational diffusion coefficient of a dimer.³⁶

The flux between dimer states is given by the following equations:

$$\begin{aligned}
 \frac{\Delta c_{AA}(t)}{\Delta t} &= f_{AA} B(t) \sum_{t'} \Delta c_{AD}(t') p_{AD \rightarrow AA}(t-t') - \sum_{t'} \Delta c_{AA}(t') p_{AA \rightarrow AD}(t-t'), \\
 \frac{\Delta c_{AD}(t)}{\Delta t} &= \sum_{t'} \Delta c_{AA}(t') p_{AA \rightarrow AD}(t-t') - f_{AA} B(t) \sum_{t'} \Delta c_{AD}(t') p_{AD \rightarrow AA}(t-t') - (1-f_{AA}) \sum_{t'} \Delta c_{AD}(t') p_{AD \rightarrow DD}(t-t') + E \\
 \frac{\Delta c_{DD}(t)}{\Delta t} &= (1-f_{AA}) \sum_{t'} \Delta c_{AD}(t') p_{AD \rightarrow DD}(t-t') - B(t) \sum_{t'} \Delta c_{DD}(t') p_{DD \rightarrow AD}(t-t') + c_0 p_{0 \rightarrow DD}(t),
 \end{aligned}
 \tag{5}$$

where f_{AA} is the fraction of isolated particles in the AD state that will enter the AA state as $t \rightarrow \infty$. f_{AA} is determined from the experimental data by the overall fraction that enter AA from AD .

These kinetic equations are solved numerically using the measured probability distributions for both monomers and dimers. The two systems are compared at the same total monomer concentration, i.e., the number concentration of dimers is half that of the monomers. In the following section we compare the two-particle transition probabilities to experimental observations of both monomers and dimers.

Results

The kinetic equations introduced in the previous section provide a general approach towards analyzing transition distributions measured in experiments. We first investigate the effect of shape on the sphere-wall interaction potential by using the heights sampled by the spheres to determine the interaction potential for monomers and dimers.³⁷ We analyze the same data to measure the dwell times in each state, which are then used to determine the transition probability distributions. Monomers are used in order to give a control system which dimer transitions can be compared. Deviations between the two systems demonstrate how size and shape alters particular transitions. Modeling the evolution of surface coverage shows the overall impact of these transition probability changes on adsorption.

Interaction Potential

The resolution of holographic microscopy is in the range of less than 10 nm for single particles and less than 30 nm for dimers.^{19,21} While this does not achieve the 1 nm resolution of height measurements using Total Internal Reflection Microscopy (TIRM), holographic microscopy can track particles over a 50 μm range compared to a range of a few 100 nm with TIRM. Tracking the entire particle trajectory represents the full range of positions accessible by the particle. The interaction potentials for monomer and dimer particles over a 5 μm separation distance are shown in Figure 2. The linear gravitational potential for the single particle is clearly visible and fits theoretical predictions well.

The interaction potential for the monomer is compared in Figure 2(a) to the combined electrostatic, depletion, and gravitational energies given in Eq.(1). The measured and

theoretical interaction potentials are matched at the inner well minimum in order to determine a reference height relative to the glass surface, $h = 0$, for the measured particle positions.

For the dimer, we report the interaction potential for each component sphere individually (Figure 2(b)). Effects of the connection between the spheres are nevertheless apparent. First, since the overall mass of the dimer is doubled, the slope of the potential at large distances is approximately twice that of the monomer. Second, within a $2\mu\text{m}$ region close to the inner well, the potential is effective reduction because many such desorbed spheres are confined in the AD state. Finally, and less significantly, the lower resolution tracking of dimers verses monomers prevents sharp resolution of the “adsorbed” well and the adjacent small barrier.

The theoretical interaction potential for the dimer is determined by multiplying the probability of a monomer at a given height by the probability of an adjoined monomer located at a center-to-center distance of $2a$. Integration over the spherical shell surrounding the monomer yields a potential that includes the effect of both particles, this increases the likelihood that a particle will be within the $2a$ distance from the inner well location.

Transitions

We first establish the escape probability distributions for monomers and compare them to theoretical predictions. As we demonstrated in previous work,¹⁸ we can compare the timescales extracted from the fits to predictions based on the interaction potentials. Figure 3 compares measurements to theoretical predictions with error bars determined from the Kaplan-Meier estimator.³⁸ The $A \rightarrow D$ transition shows good agreement with the exponential distribution predicted by Kramers' theory. The $D \rightarrow A$ also shows good agreement with the theory for diffusion within a linear potential with a reactive boundary conditions.

The cumulative escape probability distributions for the dimer shown in Figure 4 are separated by transitions into and out of the AD state. The escape probability for each transition into the AD ($AA \rightarrow AD$ and $DD \rightarrow AD$) must go to 1 as $t \rightarrow \infty$ because that is the only possible transition out of these states. For transitions out of the AD state there are two possible escapes ($AD \rightarrow AA$ and $AD \rightarrow DD$), therefore the sum of the two escape distributions must equal 1 as $t \rightarrow \infty$. The solution conditions control whether the $AD \rightarrow AA$ or $AD \rightarrow DD$ is preferred. We have adjusted the solution conditions so that the probability of adsorption and desorption are comparable, which is convenient to observe many transitions.

Although we do not make assumptions about the escape probability distributions for the dimers, we can gain some insight about the particle behavior by looking at the measured distributions. For example, an exponential distribution suggests Arrhenius behavior where the diffusion timescale within the well is short. The desorbing transitions shown in Figure 4, $AA \rightarrow AD$ and $AD \rightarrow DD$, show good agreement with an exponential distribution, as expected for escape from a deep narrow potential well. This result suggests that the desorption of a either side of the dimer is not influenced by the presence of a neighboring particle at roughly the same height. For these transitions, the near wall interactions (i.e. $h < a$) dominate the kinetics.

The adsorption transitions ($DD \rightarrow AD$ and $AD \rightarrow AA$), however, are not as easily described because they have non-negligible diffusion timescales associated with adsorption. In particular, when the dimer is in the AD state, the dimer must rotate to allow the particle to adsorb. While this local blocking effect may limit adsorption, connectivity might also enhance adsorption, because the desorbed particle is also constrained to be within approximately a distance of $2a$ from the surface, whereas a separate monomer can explore distances far from the surface. In addition, the orientation of the dimer as it adsorbs to the surface ($DD \rightarrow AD$) introduces uncertainty in predicting which subsequent transition is more likely. If the dimer adsorbs with its major axis perpendicular to the surface, it must rotate $\pi/2$ radians in order to adsorb to the AA state. In this case there is an increased chance that the dimer will desorb back to the DD state. If it happens to adsorb with its major axis nearly parallel to the surface, there is a high possibility of a rapid adsorption to the AA state.

The same approach comparing two isolated monomers to the dimers is used to look at the other transitions. We do not observe a significant difference for desorption events, i.e., $AA \rightarrow AD$ and $AD \rightarrow DD$. The other adsorption transition $DD \rightarrow AD$ also shows deviations between the monomer and dimer systems. Figure 5 shows very similar behavior at early times but a slight divergence at long dwell times. The early time behavior is dominated by the readsorption of the recently desorbed particles and so the dimer's shape will have a negligible effect. The long dwell times seen in the $DD \rightarrow AD$ transition represents periods where the particle diffuses far from the interface. Very long duration events are more likely for dimers because both particles are taken far from the interface, while it is less likely for two independent monomers to take long excursions away from the surface simultaneously.

The adsorption kinetics of monomers and dimer can also be compared by considering the time for a second particle to adsorb after a first particle adsorbs. For the dimers, this is the $AD \rightarrow AA$ transition while for the monomers the second particle is isolated and independent of the first. Figure 5 (b) compares the $AD \rightarrow AA$ transition of two independent monomers with dimers. A more rapid adsorption is observed at earlier times for dimers. The time for the second particle to adsorb will depend on its initial height. For dimers, the desorbed particle will always have an initial height closer than $2a$ while an isolated desorbed monomer will have a wide distributions of initial heights. This localization increases the dimer adsorption rate at early times, although the overall effect on the $AD \rightarrow AA$ transition is minimal: the fraction of AD particles entering the AA state, f_{AA} , increases from 0.45 for monomers to 0.48 for dimers. The enhanced adsorption due to localization is offset by the slower process of dimer rearrangement. These effects can only be seen in the probability distributions and not the net fraction of particles entering AA or DD states.

Adsorption

To gain better insight into how the monomers and dimers differ in terms of adsorption, the kinetic equations, Eq.(4) and Eq.(5), are solved using the measured probability distributions. We compute the evolution of surface area concentration, θ , from an initially uncovered surface for different values of total concentration. For dimers, the surface area coverage is computed as $\theta = 2c_{AA} + c_{AD}$. We also consider the surface mass coverage, which we define as the total number of spheres attached to the surface. In terms of mass, the contribution to

surface coverage from the AD state is doubled; the surface mass coverage is computed by $\theta_M = 2c_{AA} + 2c_{AD}$.

The difference between the two dimer blocking models defined earlier demonstrates how shape can affect surface coverage. In particular, the different descriptions of the “weakly adsorbed” AD state significantly changes adsorption kinetics. The B2 model assumes that when the particle is in the AD state, despite only one side being adsorbed, the particle will block two sites on the surface. This model assumes that the major axis of the dimer is more likely to be nearly parallel to the surface. In contrast, B1 is better represented by a dimer that is oriented perpendicularly to the surface. Viewed in this way, the B1 and B2 models represent two extremes of how dimers block the surface and alter dimer adsorption.

We first compare the surface area and surface mass isotherms of monomers and the two dimers blocking models. Figure 6 shows that both dimer blocking models result in a lower surface area coverage than monomers. At low concentrations, the difference between the monomer and dimer models is small, which indicates that differences in interaction energy, see Figure 2, have a negligible effect on adsorption. A more substantial difference in the interaction potential would be needed to more dramatically change equilibrium surface coverage at low concentrations. The equilibrium surface area coverage of both B1 and B2 dimers are nearly identical at low concentrations because there is no significant effect of blocking. However, the difference between the B1 and B2 blocking models is apparent at higher concentrations as the B2 dimers reach a plateau close to $\theta = 0.5$, while the other systems reach nearly complete surface coverage. As total concentration is increased, the surface area coverage of B1 dimers agrees more closely with monomer because the description of blocking for these two systems is similar, i.e., only adsorbed spheres block the surface. The B2 dimers demonstrate that blocking can severely limit surface area concentration, particularly if the dimer blocks the surface but does not occupy those sites.

In contrast to surface area coverage, dimerization leads to a higher mass coverage compared to monomers (see Figure 6). This is particularly true for the B1 dimer, which only blocks adsorbed sites and can more easily pack the surface. This can be understood by considering the concentration of each dimer state as a function of total concentration shown in Figure 7. As surface concentration reaches a maximum nearly all dimers on the surface will be in the AD state for both dimer blocking models. Although for the B1 system, a high surface concentration of AD dimers can densely pack the surface and essentially create a bilayer of end-on dimers. As a result, the B1 dimer mass coverage can exceed the maximum coverage of a monolayer by factor of 2. The B2 dimer cannot fully pack the surface because the AD state blocks two surface sites. In this case, the surface is partially covered with AD dimers and has a similar mass to a monolayer of monomers.

The effect of blocking can also be seen by comparing the equilibrium concentrations of AA and AD particles. The concentration of the AD state is monotonically increasing with total concentration while the coverage from AA particles reaches a maximum at around $c_T = 1$ and then decreases. This shows the limit where surface blocking becomes significant and the surface coverage becomes dominated by AD particles. The increase in blocking for the B2

system results in a lower maximum AA concentration which reach that maximum at a lower total concentration.

Using the kinetic model derived from the measured probability distribution provides a method for understanding the evolution in surface coverage from an initial uncovered surface. Examples of the surface area coverage evolution are shown for both low and high total concentrations in Figure 8. The contribution to surface area coverage from the AA and AD states are also shown in order to see how each state contributes to coverage. Because the kinetic model does not allow a transition from the DD to AA state, the dimers first transition into the AD state before reaching the AA state.

As discussed above, the difference between the dimer blocking models at low concentration is negligible and both dimers models result in a lower surface area coverage compared to monomers. At this concentration the equilibrium contributions to surface area coverage from AA and AD states are comparable. The evolution of surface coverage shows negligible nonmonotonic behavior, which indicates that the particles have sufficient time to equilibrate as they adsorb to the surface.

At high concentrations the evolution of coverage is more complex, exemplified by the nonmonotonic overshoot observed for each system. This can be understood by considering the pathway for dimer adsorption. As the dimers initially adsorb, there is enough open surface area to transition into the AA state. Subsequently, when those particles desorb and try to re-adsorb, the surface coverage has increased and the AD state is blocking from reentering the AA state. This overshoot, which is particularly noticeable in the AA state, results in a slight overshoot in the overall surface coverage.

Conclusion

In this study we use micrometer-sized colloid particles to investigate the effect of shape on adsorption by comparing the kinetics of monomer and dimer colloids. Holographic microscopy is used to track the 3-D positions of individual isolated particles over long trajectories. These trajectories are analyzed to construct distributions that describe time dependent probability for transitions between adsorbed and desorbed states. The probability distributions are then used in kinetic equations to understand how the adsorption of dimers will differ from monomers.

The results show that depending on how surface coverage is defined (by mass or area), the dimers can either enhance or suppress adsorption in comparison to monomers. Dimers enhance surface mass coverage but suppress surface area coverage. Surface area blocking is considered by two extremes. In either case, the concentration of adsorbed particles becomes increasingly occupied by partially adsorbed (AD) particles as concentration increases, to such an extent that at high concentration the steady state concentration of AA is zero. The AA state is only significant at intermediate time or intermediate concentration.

This approach shows that the structure of the adsorbed layer depends significantly on concentration. It also illustrates that a direct measurement of particle transition probabilities enables a prediction of adsorption without a detailed model of the underlying mechanics.

This method therefore directly models the “reaction” with the surface. This method could also be applied to understand the evolution of coverage for reversibly adsorbing molecules, such as proteins, by tracking the lifetimes of adsorbed and desorbed states of an individual molecule.^{9,39} While this is a simplified picture compared to an adsorption experiment because it assumes no interaction between adsorbed species, it demonstrates that the effects of cooperation or blocking depends on the behavior of adsorbed particles. This would be realized in experiments by measuring the evolution of surface coverage for a population of dimer particles onto an initially uncovered surface. The spatial distribution and hydrodynamic interactions between particles are expected to alter the adsorption kinetics as well as equilibrium concentration, especially at high concentrations. The adsorption kinetics can also be studied in simulations where the interaction between particles can be more easily tuned.

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Figure 1.

Diagram of monomer and dimer states in relation to the wall. Monomers can be in either adsorbed (A) or desorbed (D) states. Dimers can have both spheres adsorbed (AA), one sphere adsorbed and the other desorbed (AD) or both desorbed (DD).

Figure 2.

Interaction potentials of monomers (a) and dimers (b) for in solution of 0.8 Vol % Ludox TMA and 1 mmol/L NaCl. The solid line is a theoretical fit and the dashed vertical line denotes the demarcation between adsorbed and desorbed spheres. The lower resolution tracking for the dimers results in a worse fit, particularly in the near wall region where there are larger gradients in the potential.

Figure 3. Cumulative escape probability distributions for monomer particles. The cumulative escape probability follows an exponential distribution for desorption ($T_{A \rightarrow D}$) while show the adsorption ($T_{D \rightarrow A}$) follows a nonexponential distribution. Error bars one standard deviation determined from the Kaplan-Meier estimator.³⁸

Figure 4. Cumulative escape probability distributions for all dimer transitions (symbols) and theoretical fits (lines). The dashed lines are predictions from desorption of monomers. Error bars show one standard deviation determined from the Kaplan-Meier estimator.³⁸

Figure 5.

Cumulative escape probability distributions comparing adsorption transitions of monomer and dimer: a) into and b) out of state AD . Dimers have a higher likelihood of longer $DD \rightarrow AD$ transitions (slower adsorption) than monomers (a). In contrast, dimers show a faster $AD \rightarrow AA$ transition than monomers and slightly greater overall likelihood of adsorption (b). Error bars show one standard deviation determined from the Kaplan-Meier estimator.³⁸

Figure 6.

Adsorption isotherms showing equilibrium surface concentration, θ (a) and θ_M (b), as a function of initial concentration for monomers, dimers with single blocking (B1), double blocking (B2), and double blocking with double coverage from AD (B2 2xAD). The results are compared to a Langmuir isotherm, $\theta = kc_T/(1+kc_T)$, with equilibrium constant $k = 0.5$ for reference.

Figure 7. Adsorption isotherms of dimer adsorbed states as a function of initial concentration. The surface coverage of each dimer state are shown for each of the blocking models.

Figure 8.

Comparison of monomer and dimer surface area coverage evolution for two values of initial monomer concentration, $c_T = 0.1$ (left) and $c_T = 10$ (right). The surface area coverage for dimers is calculated by summing adsorbed spheres, $\theta = 2c_{AA} + c_{AD}$. Dimer area coverage is shown with single blocking (B1), double blocking (B2). The contributions to surface area coverage from the AA and AD states are plotted in dashed and dash-dot lines respectively.