A Colloid Model System for Interfacial Sorption Kinetics

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Supporting Information

ABSTRACT: Particle adsorption to an interface may be a complicated affair, motivating detailed measurements of various processes involved, to discover better understanding of the role of particle characteristics and solution conditions on adsorption coverage and rate. Here we use micron size colloids with a weak interfacial interaction potential as a model system to track particle motion and measure the rates of desorption and adsorption. The colloid-interface interaction strength is tuned to be less than 10 $k_B T$ so that it is comparable to many nanoscale systems of interest such as proteins at interfaces. The tuning is accomplished using a combination of depletion, electrostatic, and gravitational forces. The colloids transition between an entropically trapped adsorbed state and a desorbed state through Brownian motion. Observations are made using an light-emitting diode (LED)-based total internal reflection microscopy (TIRM) setup. The observed adsorption and desorption rates are compared to theoretical predictions based on the measured interaction potential and near-wall particle diffusivity. The results demonstrate that diffusion dynamics play a significant role when the barrier energy is small. This experimental system will allow for the future study of more complex dynamics such as nonspherical colloids and collective effects at higher concentrations.

INTRODUCTION

Adsorption of molecules to interfaces is sensitive to the interaction potential between them. This relationship is relevant in many biological systems (i.e proteins, vesicles, nanoparticles) and in industrial applications such as coatings, filtration, and paper making. Measurements of the interaction potential and kinetics of nanoscale molecules is challenging due to the difficulty of tracking individual molecules. Recent advances have enabled single molecule tracking of adsorbed molecules which can extract waiting times and displacements between adsorption events. While these experiments extract important information about the interfacial kinetics of nanoscale molecules, the energy landscapes are not directly measured, and behavior can only be inferred through observations of waiting time distributions.

To gain better insight into the kinetics of nanoscale systems, we present a micron-sized model colloidal system capable of long duration single particle tracking while simultaneously measuring the interaction potential. While these spherical colloids are larger than nanoscale molecules, the model system allows for the direct comparison of measured adsorption and desorption probability distributions with theoretical models derived from the interaction potential.

Micron-sized colloids have also been used to study kinetics in double well potentials typically created by optical traps as well as for studying nanoscale interaction potentials between surfaces, including electrostatic, steric, and depletion interactions. In contrast to these experiments, the dynamics of individual particles in a double-well interaction potential with a planar surface is relatively unexplored. In general, producing a double well interaction potential between two surfaces requires overlapping attractive and repulsive interactions. The dependence of adsorption and desorption rates on the interaction potential have been studied in the context of particle separation technologies. Colloids serve a useful model system for studying such dynamics. One such system uses charged colloidal silica to produce a depletion attraction at short distances, in addition to a weaker repulsive interaction just beyond the attractive region. This repulsive interaction is attributed to a layering effect of the charged depletant. The two-well potential is therefore a combination of forces; the near wall well is a balance between electrostatic repulsion and depletion attraction, while the other well is a balance between electrostatic repulsion and gravitational attraction.

Our approach utilizes combined total internal reflection microscopy (TIRM) and epifluorescence microscopy to track the motion of individual micron-sized particles near an interface with high resolution as they adsorb and desorb from the interface in a double-well potential. Specifically, in an “on” state, the particle is adsorbed or relatively tightly bound to the surface, and in the other “off” state, the particle is desorbed and explores a much larger volume. The location and strength of the potential wells are tuned by adjusting the relative strength of the depletion, electrostatic, and gravitational forces. This can primarily be achieved by adjusting the particle size, screening length, and depletion concentration. The strength of the depletion attraction can be adjusted to alter the characteristic barrier crossing frequency. In addition, the influence of the wall on particle mobility also varies the rate at which particles cross.

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We aim to demonstrate how the distribution of crossing times between two wells separated by an energy barrier depends on the shape of the potential wells and the barrier height. First, we discuss the theoretical models for transitions over potential barriers and then introduce the materials and methods relevant for particle tracking using an LED-based total internal reflection microscopy setup. The particle tracking data is then analyzed statistically, to determine the interaction potentials between a particle and the surface, a result that is compared to the theoretical model developed by Sharma and Walz. The particle trajectories are analyzed in context of the measured interaction potentials to determine the dwell time distributions within the potential. The measured dwell time distributions are compared to theoretical transition models for each interaction potential.

## THEORY

### Interaction Potential

The double-well interaction potential is produced by a sum of depletion, electrostatic, van der Waals interaction, and gravitational potentials:

\[
U_{\text{tot}} = U_{\text{dep}} + U_{\text{el}} + U_{\text{vdw}} + U_{g}
\]

The interaction potential between the particle and the glass surface produced by a charged depletant is calculated using a force balance approach developed by Sharma and Walz (see Supporting Information for details). The electrostatic interaction potential between a particle and wall is given by

\[
U_{el}(h) = 4\pi\varepsilon_0 \varepsilon (k_b T/e)^2 a Y_2 \exp(-\kappa h)
\]

where \( h \) is the distance between surfaces, \( a \) is the particle radius, \( \varepsilon \) is the relative relative permittivity of the medium, \( \varepsilon_0 \) is the vacuum permittivity, \( e \) is the elementary charge, and \( Y_1 \) and \( Y_2 \) are the effective surface charges of the particle and wall, respectively. \( \kappa \) is an adjusted inverse Debye length introduced due to the enhanced screening caused by the charged silica. The van der Waals interaction between a sphere and a flat surface where \( h \ll a \) can be described using the Derjaguin approximation:

\[
U_{\text{vdw}}(h) = -2\pi a \int_0^\infty \frac{A(h')}{12nh^2} dh'
\]

where \( A(h) \) is the Hamaker function from the Lifshitz theory calculated using measured material parameters. The gravitational potential energy is given by

\[
U_g(h) = \frac{4}{3} \pi a^3 \left( \rho_p - \rho_b \right) g h
\]

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

The particle positions are used to determine an experimental potential profile by inverting the Boltzmann distribution:

\[
\frac{U_{\text{exp}}(h)}{k_B T} = \ln \left[ \frac{p(h_{\text{max}})}{p(h)} \right] + \frac{C}{k_B T}
\]

where \( p(h) \) is the probability of finding the particle at a distance \( h \) and the wall, and \( h_{\text{max}} \) is the particle position with the highest probability.

As will be discussed in the following, a number of issues must be addressed with care to determine the true particle elevation. The particle—wall distance is determined by matching the bottom of the depletion well from the theoretical model and the experimental data using an ensemble TIRM technique. The barrier position determined from the potential is used to define the two well domains.

### First Passage Time

The probability describing a particle position relative to the wall in time, \( p(h,t) \), is given by the Smoluchowski equation:

\[
\frac{dp(h,t)}{dt} = \frac{\partial}{\partial h} \left[ D(h) \left( \frac{dp(h,t)}{dh} + \frac{\partial U}{\partial h} \right) - p(h,t) \right]
\]

where \( D(h) \) is the position-dependent diffusivity and the initial position is given by

\[
p(h, t = 0| h_0) = \delta(h - h_0)
\]

The first passage time distribution describes the probability of a particle crossing a particular point given an initial starting condition, \( h_0 \). This can be achieved by solving for the conditional probability with an adsorbing boundary where particles are removed from the domain. The integral of the conditional probability gives the probability of the particle surviving within a domain as a function of time. Hence, the probability of the particle escaping from the well at \( t \) is given by

\[
T(t) = 1 - \int_{h_0}^\infty p(h, t|h_0) \, dz
\]

where \( h \) is the domain from which the particle escapes.

Concise analytic results for \( p(h,t|h_0) \) are limited to special cases for the potential, such as linear and quadratic potentials, and assume uniform diffusivity. In order to gain insight into the important quantities regulating the crossing time distributions, we approximate and discretize the potential and diffusivity landscapes in the two well system in order to make an analytical solution tractable.

A common approximate solution to eq 6, first developed by Kramers, can be made in the limit of low flux out of a potential well. This is commonly the case for escape rate from a deep and narrow potential well where the energy barrier is larger than thermal energy, \( \Delta U \gg k_B T \), similar to the “on” well shown in Figure 1. Applying Kramers’ approach requires a separation of time scales such that the time scale of escape is the longest time scale, which implies that all other time scales

![Figure 1. Theoretical potential profile for 0.5 mmol/L NaCl, 0.5 vol % Ludox TMA, and 1.5 μm radius polystyrene particle. The barrier maximum defines whether the particle is in the “on” or “off” region.](image-url)
must be shorter. In particular, the relaxation time within a potential well must be shorter than the escape time. The relaxation time is a rough measure of the time it takes for a particle to explore the domain of the potential well.

The relaxation time can be estimated by the diffusion time scale within the well,

\[ \tau_D = \frac{L_w^2}{D_L} \tag{9} \]

where \(D_L\) is the diffusivity perpendicular to the interface in the well region, and \(L_w\) is the characteristic width of the well. The length scale of the two wells differ between \(L_{well\,on} \approx 100 \text{ nm}\) for the “on” well and \(L_{well\,off} \approx 1 \mu\text{m}\) for the “off” well. The diffusion time scale is to be compared to the characteristic time for crossing the barrier,

\[ \tau_b = \frac{L_{barrier}^2 \Delta U/k_bT}{D_L} \tag{10} \]

where \(L_{barrier} = R_\text{ell} - h_{on}\) is the width of the barrier (see Figure 1). The diffusivity is determined using theoretically determined perpendicular diffusivities within the well region. Measuring the perpendicular diffusivity is made difficult by the influence of the interaction potential with the wall. We choose to measure the hindered mobility of particles through the observed parallel diffusivity and then use theoretical perpendicular diffusivity coefficients corresponding to the measured parallel diffusivities. The diffusivities are found to agree with values that correspond with the approximate average height in each well (see Supporting Information). The perpendicular diffusivity in the “on” well is \(D_{L\,on} \approx 0.01 \mu\text{m}^2/\text{s}\), while further from the wall in the “off” well is \(D_{L\,off} \approx 0.05 \mu\text{m}^2/\text{s}\).

The applicability of Kramers’ theory for desorption, i.e., the “on to off” transition, is verified by showing that \(\tau_D \approx 1.0 \text{ s}\) is short compared to the barrier crossing time scale in the range \(\tau_b \approx (1 \text{ to } 100) \text{ s}\), where the barrier heights are within the range \(\Delta U/k_bT \approx (1 \text{ to } 10)\). This characteristic crossing time can be found using Kramers’ dwell time equation,

\[ \tau_K = \int_{h_0}^{h_b} \frac{dh}{D_L(h)} \int_0^h dh' \exp\left(-\beta(U(h') - U(h))\right) \tag{11} \]

where \(\beta = 1/(k_bT)\). These integrals are computed numerically from the measured potential, \(U(h)\), and the perpendicular diffusivity values for \(D_L(h)\) as noted above. With a single time scale regulating the barrier crossing, an exponential distribution with single characteristic time scale is expected for the escape probability distribution, i.e., the probability that the particle will escape from the potential well as a function of time. The experimental data are compared to the cumulative exponential distribution, \(T(t) = 1 - \exp(-at + h_0)/2\sqrt{Dt}\) where \(\tau_{on}\) is the characteristic time to be fit from experimental data. These values are then compared to \(\tau_b\) used eq 11 and the measured interaction potential.

In contrast to the behavior of a particle in a deep and narrow well, a particle released in a broad and shallow well will have a relatively long relaxation time and a short barrier crossing time scale. Therefore, it is not expected that the “off to on” transition (adsorption) will satisfy the conditions for Kramers’ theory. Repeating the time scale analysis for the “off” well shows that the characteristic diffusion time is longer due to the wider well, \(\tau_D \approx (10 \text{ to } 100) \text{ s}\), and the barrier crossing time scale is much shorter, \(\tau_b \approx (0.01 \text{ to } 1) \text{ s}\), because the outer barrier is comparable or smaller than thermal energy, \(\Delta U/k_bT \approx (0 \text{ to } 2)\). The long diffusion time scale and a short barrier crossing time scale demonstrate that the diffusion within the well must be included in the description of the escape probability distribution.

An analytic solution for the probability distribution is found by approximating the outer well as a linear potential produced by gravity. The barrier for passage into the “on” well is described by a reactive boundary condition,

\[ D \frac{\partial}{\partial h} \left( \frac{1}{\partial h} \frac{\partial U}{\partial h} \right) p(0, t) = K p(0, t; h) \tag{12} \]

where \(K\) is a reaction rate constant that regulates the adsorption of particles at the boundary. If \(K = 0\), the boundary condition is purely reflective, while as \(K \to \infty\) the boundary becomes purely adsorbing.

The reactive boundary describes how a particle approaching the potential barrier can either complete a crossing into the “on” well or return to diffusing in the outer potential well. A large barrier is expected to have a lower value for \(K\) and be more reflective, while a small barrier will have a higher \(K\) and behave similarly to a purely adsorbing boundary. We use the solution of Smoluchowski’s equation in a linear potential with a reactive boundary at the origin to determine the escape probability distribution, i.e., the probability the particle will escape from the potential well as a function of time. The cumulative escape probability distribution is found by integrating this expression in eq 8 to yield

\[ T(t) = 1 - \frac{1}{2} \left( 1 + \text{erf} \left( \frac{-at + h_0}{2\sqrt{Dt}} \right) \right) - \frac{K}{2(K - \alpha)} \text{erf} \left( \frac{at + h_0}{2\sqrt{Dt}} \right) + \frac{2K - \alpha}{2(K - \alpha)} \text{erf} \left( \frac{2Kt - at + h_0}{2\sqrt{Dt}} \right) \tag{13} \]

where \(\alpha = F D_L/k_bT\) and \(F\) is the slope of the linear potential. In the experimental system, particle mobility varies with height, and therefore the diffusivity used in eq 13 must be approximated by a constant value.

**Experimental Section**

**Imaging.** The particles are tracked using a combined total internal reflection microscopy (TIRM) and epifluorescence microscopy on an Olympus IX71 inverted microscope using 60x water (1.2NA) objective with 1.6× magnification. [Note: Certain 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.illumination is switched each frame between TIRM and epifluorescence using an Arduino Uno controller through a trigger generated by the EMCCD camera (PhotonMax S21d Princeton Instruments) at 20 ms intervals using 4×4 binning. Although switching between TIRM and epifluorescence images reduces the effective frames per second by half, this approach uses the advantages of each imaging mode; epifluorescence is used for tracking the lateral position (in X and Y), and TIRM imaging is used for tracking separation from the surface (in Z). In contrast to typical TIRM setups, such as prism or objective based methods, we employ an LED waveguide-based method similar to the setup recently developed by Ramachandran et al. The

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covariance acts as an optical waveguide using edge illumination from the surrounding LEDs, spaced 1 cm from the coverslip edge, allowing only light undergoing total internal reflection into the chamber.

Our setup uses a single 22 mm glass coverslip (refractive index =1.52) as the bottom of a closed chamber. The coverslip is sealed between two 20 mm Viton rubber washers using Krytox vacuum grease (Dupont, refractive index =1.30). The chamber is surrounded by a 4 cm diameter ring of six monochromatic LEDs (Luxene Star-SR-05-M0100-530 nm) mounted on a frame constructed from copper and tubing connected to chilled water from a refrigerated circulating bath (Endocal ETC-58). Before being assembled, the coverslips are sonicated in 100% ethanol for 30 min, 30 min in NaOH, and rinsed with Millipore water.

The evanescent wave intensity for the LED-TIRM setup (Figure 2) is measured. Similarly, Ramachandran et al. (2013) measured the intensity of a fluorescent bead as it was moved away from the surface and found a decay depth of 200 nm when fit with a single exponential. We performed a similar calibration on our setup using a microcapillary connected to a piezo positioning stage. The capillary is mounted on a piezo stage above the chamber, and a 10 μm particle is held onto the end of the capillary using suction. Images are recorded at each location as the capillary is moved in 5 nm increments toward the glass. Contact between the particle and the glass can be observed by a constant lateral movement of the particle. The intensity is normalized by the mean intensity at zero height. The measurement is repeated using different polystyrene spheres and the results are aggregated to obtain an averaged intensity as a function of distance.

The integrated intensity, \( I \), is measured from the trajectory data and compared to theoretical crossing time distributions. The exact time from these domains is measured from the trajectory data and compared to theoretical crossing time distributions. The effect of parameters is further investigated for the "off" well model.

In this section we analyze particle height trajectories to determine the interaction potential for different bulk solutions. An example of a particle height trajectory is shown in Figure 4. The interaction potential is used as a reference for determining "on" and "off" domains. The crossing time from these domains is measured from the trajectory data and compared to theoretical crossing time distributions. The effect of parameters is likely due to higher order layering effects not captured by the theory.

As expected from theory, increasing the depletion concentration increases the magnitude of both inner and outer barriers. The range of depletion concentration used for each salt concentration is chosen to produce similar inner well depths, in the range of \( \Delta U_{in} \approx 4-7 k_B T \). For the outer barrier, the lowest depletion concentrations produce a barrier of negligible magnitude that increases with concentration until comparable with thermal energy \( \Delta U_{diff} \approx k_B T \). The 1.0 mmol/L NaCl system produces a larger outer barrier than the 0.5 mmol/L NaCl system, even though the inner well heights are comparable for both systems. The experimental dwell time distribution in Figure 6 shows good agreement with the cumulative exponential distribution expected from Kramers’ theory. A comparison between the measured and predicted dwell times are shown in Table 2. As a result of using an

\( h = -\lambda \ln(I/I_{max}) + h_{diff} \)
As discussed in the Theory section, the escape probability from the “off” well is not expected to fit the assumptions of Kramers’ theory due to the large width of the well and the small barrier magnitude. Instead, the measured dwell times are fit using eq 13 for the rate constant $K$. An estimate of the barrier crossing time scale can be made by considering the length scale over which the reaction occurs by $\tau_{\text{off}} = L_{\text{barrier}}/K$, where the width of the barrier is the same as before, $L_{\text{barrier}} = h_{\text{barrier}} - h_{\text{on}}$.

A comparison of measured values with eq 13 is shown for the “off” to “on” transition in Figure 7. The agreement between the measured data and theory shows that eq 13 adequately describes the escape from the outer well. In particular, the model captures the long tail behavior not captured by a simple exponential, also shown in Figure 7 for comparison. This exemplifies that both diffusion and barrier crossing time scales are important to describe the transport out of the “off” well.

Figure 7 demonstrates that the form of the purely adsorbing boundary is nonexponential (see dotted line), and the experimental results also show slower transitions than the purely adsorbing case. The data in Figure 7 are fit with finite value of $K$ that shift the escape probability distribution toward longer times. The systems with larger barriers are fit with smaller values of $K$, corresponding to a larger characteristic crossing time. The 1.0 mmol/L NaCl system, shown in Figure 7b, shows a greater delay in the escape probability distribution as depletion concentration is increased. This corresponds to a greater increase in barrier height as depletant concentration is increased (see Figure 5b). In contrast, the increase in the barrier height with depletion concentration is noticeably smaller for the 0.5 mmol/L NaCl system seen in Figure 5a. The lack of

<table>
<thead>
<tr>
<th>NaCl (mmol/L)</th>
<th>Ludox (vol %)</th>
<th>$h_{\text{barrier}}$ (nm)</th>
<th>$h_{\text{on}}$ (nm)</th>
<th>$h_{\text{off}}$ (nm)</th>
<th>$\Delta U_{\text{on}}$ ($k_BT$)</th>
<th>$\Delta U_{\text{off}}$ ($k_BT$)</th>
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<tr>
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<td>178 ± 11</td>
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<td>218</td>
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<tr>
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<tr>
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<td>0.7 ± 0.2</td>
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<td>83</td>
<td>163</td>
<td>7.0 ± 0.2</td>
<td>1.0 ± 0.2</td>
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*The locations of the potential barrier are denoted as $h_{\text{barrier}}$ with 95% confidence bounds from the fit. The height locations used to determine entry and exit from the potential wells are denoted $h_{\text{on}}$ and $h_{\text{off}}$ and are offset from the barrier by 40 nm. The barrier height for the “on” and “off” wells are given by $\Delta U_{\text{on}}$ and $\Delta U_{\text{off}}$ with 95% confidence bounds from the fits.

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Figure 4. Particle–wall distance as a function of time for system of 1.0 mmol/L NaCl, 0.6 vol % Ludox TMA. The dashed line indicates the location of the barrier peak and the dotted lines indicate the entry positions for each well.

ensemble interaction potential measurement, polydispersity of particle properties and errors in the interaction potential measurement may cause discrepancy between $\tau_{\text{on}}$ and $\tau_{\text{off}}$. The effect of the exponential term from eq 10 is seen in the rapid increase in the characteristic dwell time with barrier magnitude.\(^{44}\) Further increase in the depth of the “on” well would result in very long waiting times ($\tau_{\text{on}} \approx 100$ s) between desorption events. The agreement with Kramers’ theory over the $\tau_{\text{on}} \approx 1–100$ s range suggests that the same behavior would continue at even greater barrier magnitudes.

Figure 5. Comparison of experimental and theoretical potential profile for (a) 0.5 mmol/L NaCl and (b) 1.0 mmol/L NaCl. The potentials are using $\Phi_1 = \Phi_2 = 60$ mV. The inverse Debye length for 0.5 mmol/L NaCl was adjusted to $\kappa^{-1} = 11.0$ nm from an original value of $\kappa^{-1} = 13.6$ nm. The inverse Debye length for 1.0 mmol/L NaCl was adjusted to $\kappa^{-1} = 7.8$ nm from an original value of $\kappa^{-1} = 9.6$ nm.
a significant increase in barrier height with added depletant in the 0.5 mmol/L NaCl system leads to little change in the outer well escape probability distribution seen in Figure 7a. The fit values of $\tau_{\text{on}}$ are compared to the approximate barrier crossing time scale, eq 10, using the same length scale, perpendicular diffusivity values at the barrier, and barrier heights from Table 3. The values show fairly good agreement in the magnitude of the time scale and increase with barrier height.

Table 2. Comparison of Characteristic Dwell Times in the "On" Potential Well between Measured Data and Predictions Using Eq 11

<table>
<thead>
<tr>
<th>NaCl (mmol/L)</th>
<th>Ludox (vol %)</th>
<th>$\tau_K$ (s)</th>
<th>$\tau_{\text{on}}$ (s)</th>
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</thead>
<tbody>
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<td>0.3</td>
<td>0.3</td>
<td>5.8±0.6</td>
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</tr>
<tr>
<td>0.5</td>
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<tr>
<td>1.0</td>
<td>0.6</td>
<td>73.1±14.6</td>
<td>62.9±3.5</td>
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"$\tau_K$ is predicted by integrating the measured interaction potential with error estimated from the uncertainty in the measured potential given in Table 1. $\tau_{\text{on}}$ is the time constant determined from fitting the measured cumulative escape probability to an exponential distribution with corresponding 95% confidence interval from the fit.

The fit values of $\tau_{\text{off}}$ are compared to the approximate barrier crossing time scale, eq 10, using the same length scale, perpendicular diffusivity values at the barrier, and barrier heights from Table 3. The values show fairly good agreement in the magnitude of the time scale and increase with barrier height.

Table 3. Comparison of Characteristic Dwell Times in the "Off" Potential Wells between Measured Data and Predictions from the Interaction Potential Using $T(t)$ (See Eq 13)

<table>
<thead>
<tr>
<th>NaCl (mmol/L)</th>
<th>Ludox (vol %)</th>
<th>$\tau_K$ (s)</th>
<th>$\tau_{\text{off}}$ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3</td>
<td>0.3</td>
<td>0.53±0.06</td>
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<tr>
<td>0.5</td>
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</tbody>
</table>

"The estimated time scale is determined from eq 10. The measured time scale is determined by the fitted value of $K$ by $\tau_{\text{off}} = L_{\text{barrier}}/K$.

The shift in the escape probability distributions as depletion concentration is increased, particularly for the 1.0 mmol/L system, demonstrates an opportunity for temporal scaling. The fitted crossing time scale, $\tau_{\text{off}}$, is primarily responsible for

Figure 6. Exponential dwell time distribution for desorption, i.e., paths from "on" well to "off" well, for (a) 0.5 mmol/L NaCl and (b) 1.0 mmol/L NaCl. The data are binned into 30 equally spaced bins and fit to a cumulative exponential distribution (dashed lines). Error bars represent ±2 standard deviations in the whole text. Here error is based on the square root of the bin count.

Figure 7. Nonexponential dwell time distribution for paths from "off" well to "on" well for (a) 0.5 mmol/L NaCl and (b) 1.0 mmol/L NaCl. The data are binned into 30 equally spaced bins and fit to $T(t)$; see eq 13. The data are fit for the value of $K$. The data for 1.0 mmol/L NaCl is shown in the inset with horizontal axis as $t/\tau_{\text{off}}$ where $\tau_{\text{off}} = L_{\text{barrier}}/K$. 
which is the same as the solution to Smoluchowski’s equation with $F = 0$ and $K_{h_0}/D_\perp < 1$. The adsorption is regulated by the relative magnitude of the exponential and error function terms, each of which scale as $D_\perp/(aK)$.

In contrast, a system with a strong linear force, such as a dense particle in a gravitation field or the electrophoretic force on a charged molecule in a uniform electric field, will have $K < \alpha$. In this case, eq 13 can be simplified to an exponential decay with the time scale $D_\perp/(\alpha K)$,

$$T(t) \approx 1 - e^{\left[-K(\alpha + h_0)/D_\perp\right]}$$

This result can be understood in context of Kramers’ theory: a narrow potential well with fast relaxation will produce an exponential escape probability distribution. The diffusion time scale within the potential will be short, and adsorption will be regulated by the barrier height, which in this context is captured by the term $K$.

**CONCLUSION**

The dynamics of microspheres in a double-well interaction potential near a wall is investigated. Microsphere positions are tracked using a combined TIRM and epifluorescence setup. The measured interaction potential is used to predict the dwell time in each potential well, which can be compared directly with the adsorption and desorption rates. The results show that the functional form of the crossing time distribution can differ from an exponential distribution and depends on the shape of the interaction potential.

The planar geometry used to create a two-well potential provides a useful model system for studying interfacial kinetics. In particular, the behavior in the outer well does not fit the assumption of Kramers’ transition theory but is well described instead by the first passage time distribution for a linear potential with a reactive boundary. This may be relevant to other systems where the potential is not easily measured, particularly where multiple time scales are present. Since study of this model system can be used to investigate adsorption phenomena in detail, this approach has the potential to elucidate the effects of particle–particle interactions and nonspherical shapes.
**ASSOCIATED CONTENT**

Additional information is provided on the charged depletion interaction potential and diffusion measurements. This material is available free of charge via the Internet at http://pubs.acs.org/.

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Notes

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