

Adsorption and diffusion in a one-dimensional potential well

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We investigate the adsorption and diffusion of colloidal particles at an interface containing a one-dimensional potential well. It is observed how the adsorption kinetics onto the wall is altered with time, and one observes the formation of a particle chain. We find that the time it takes for a bead to penetrate into the chain depends strongly on the particle density, and beyond a critical value this time diverges. We also study diffusion within the well, and find that at low particle densities the short time behavior is governed by normal Fickian diffusion.

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I. INTRODUCTION

Adsorption and diffusion are two of the most fundamental physical processes in nature, and have therefore been studied for centuries. Of particular interest are confined biological systems, where, e.g., narrow ion channels allow the passage of a restricted number of potassium and sodium ions simultaneously [1]. Traditionally, adsorption and diffusion have been studied in bulk, at surfaces or in porous media channels by, e.g., surface pressure, fluorescence correlation spectroscopy, or magnetic resonance methods [2–5]. Recently one has taken interest in direct observation of one-dimensional diffusion in colloidal model systems, and these studies have given new insights into anomalous diffusion, adsorption, and hydrodynamic interactions [6–11].

The aim of this work is to present a method for direct observation of adsorption and diffusion of particles at an interface containing a one-dimensional potential well. Previous experimental studies have been based on hard walls, fabricated by, e.g., photolithography, for confinement of the particles [6,9]. Here we use a localized magnetic potential well much smaller than the particle diameter, which makes it impossible for the particles to pass each other. It is clear that paramagnetic particles will be attracted to such a well, see Ref. [12], and this allows us to study adsorption of particles at the potential well as a function of the particle density inside and outside the chain formed at the well. Three regimes of particle dynamics can be distinguished as the paramagnetic particles interact with the well. First, there is a directed Brownian motion of the colloidal suspension in the magnetic potential, driving all particles toward the magnetic wall. Second, an additional particle arriving at the already loaded well must wait for the particles in the well to rearrange, after which it may penetrate into the chain. If the density of particles is too high, they form an impenetrable chain, though without substantially altering the speed at which new beads approach this chain, since paramagnetic

particles do not screen the magnetic field effectively. Finally, after entering the chain the particles undergo a restricted one-dimensional diffusion.

II. EXPERIMENT

The magnetic potential well was created using a bismuth-substituted ferrite garnet film of thickness $4\ \mu\text{m}$ and magnetization $M_s = 10^5\ \text{A/m}$. Due to the low uniaxial anisotropy, these garnet films have very large (0.1–10 mm) in-plane magnetized domains separated by domain walls. Here the domain wall acts as a magnetic potential well, which attracts magnetic beads in absence of external fields. A glass ring with diameter about 1 cm was put on top of the garnet film, and beads immersed in water at a density of $\sim 10^6$ beads/ml were confined within the walls of this ring. The paramagnetic beads used here have an effective susceptibility of $\chi = 0.17$ ($\pm 15\%$), and were manufactured by Dynal (Dynabeads M270), coated with a carboxylic acid (COOH—) group. Adhesion of the beads to the garnet film could be prevented by coating the garnet film using the layer by layer adsorption technique [13,14]. The coating results in electrostatic double layer repulsion between the beads and the film. Thus, although the material properties of the garnet film are fixed, the surface properties may be altered by coating the film. In this way one may simulate a wide range of different charge and adhesion properties. A more detailed description of the system can be found in Ref. [12].

Figure 1 shows the basic system under consideration. In Fig. 1(a) many particles have attached to the minimum of the potential well, while there are still some left outside it. It is seen that due to the magnetic attraction between the beads and the domain wall, the particles form a chain at the minimum of the potential well, despite the competing magnetic and electric repulsive forces between the beads. In Fig. 1(b) most of the particles have attached to the potential minimum. We observe that the chain bead density ρ of this chain increases with time, as nearby particles are adsorbed by the well. Here we define the chain bead density as the number of beads divided by the length of the well in the field of view (see also Ref. [10]). In the current study we assume that the boundaries of the chain do not influence the dynamics of the particles in the chain, i.e., an infinitely long chain. This is a reasonable first approach, since the lengths of the domain

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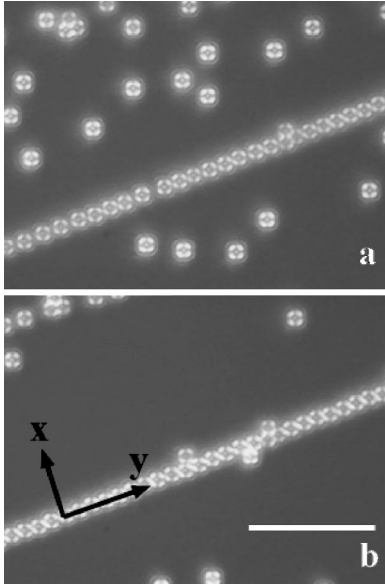


FIG. 1. Two consecutive pictures separated 180 s in time showing the adsorption process. Note that in (b) most of the beads seen in (a) are located at the line. The white bar is 30 μm .

walls are typically orders of magnitude larger than the bead diameter.

III. ADSORPTION

A. Directed Brownian motion

Let an isolated paramagnetic bead with radius a ($a = 1.4 \mu\text{m}$ in our experiments) be located at a distance x from the unloaded potential minimum, and its center at a height z above it. The width of the wall, w , is much smaller than the diameter of the beads. Due to limited optical resolution it is difficult to determine exactly, but a rough estimate gives $w \approx \pi\sqrt{A/K} \approx 300 \text{ nm}$, where A is the exchange parameter, $A \approx 10^{-11} \text{ J/m}$, and K is the anisotropy constant, $K \approx 10^{-3} \text{ J/m}^3$. In general, it is difficult to determine the width of the domain wall by conventional methods, e.g., magnetic force microscopy, due to their low coercivity (i.e., the tip of the force microscope perturbs or moves the domain wall). In a previous paper we showed that the time it takes for an isolated bead to travel to the unloaded potential minimum is given by [12]

$$t - t_0 = B\left(\frac{1}{4}x^4 + x^2z^2 + z^4 \ln|x|\right), \quad (1)$$

where t_0 is a constant and $B = 3\pi\eta f/2\mu\chi a^2(M_s w)^2$, where μ is the permeability of water, η the viscosity of water, and f the hydrodynamic drag coefficient. In Fig. 2 the star symbols show the kinetics of attraction of a single bead to an unloaded potential well. Here we find $B = 2 \pm 0.1 \times 10^{22} \text{ m}^{-4} \text{ s}$, assuming that $z \approx a$.

The attraction of consecutive beads is changed significantly upon loading the well with a dense chain of particles. Figure 2 shows the bead travel time as a function of distance from the potential minimum for two different chain bead densities. Isolated beads attracted toward the center of the

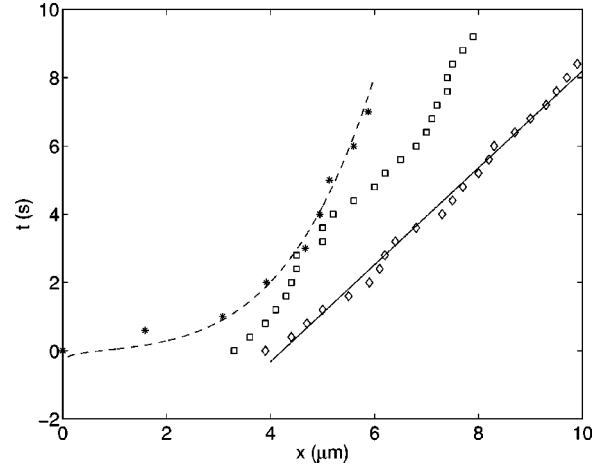


FIG. 2. The bead travel time as a function of distance from the unloaded as well as loaded potential well. The stars correspond to a bead chain density of $\rho = 0 \mu\text{m}^{-1}$, the boxes correspond to $\rho = 0.247 \mu\text{m}^{-1}$, and the diamonds correspond to $\rho = 0.288 \mu\text{m}^{-1}$. The dashed line shows the best fit of Eq. (1) when $\rho = 0 \mu\text{m}^{-1}$, whereas the solid line shows the best linear fit when $\rho = 0.288 \mu\text{m}^{-1}$. At $x < 4 \mu\text{m}$ the dynamics crosses over to the jamming dynamics discussed in Sec. III B.

potential loaded with a chain of density $\rho = 0.288 \mu\text{m}^{-1}$ travel at constant speed, $t - t_0 = x/v$ ($t_0 = -6 \text{ s}$ and $v = 0.7 \mu\text{m/s}$). This suggests that the particles already in the well smoothen the potential, thus providing a constant force over the distances studied here. A colloidal suspension of particles also drifts toward the loaded well, but with significant Brownian fluctuations arising from the particle interactions superimposed. The electrostatic repulsion from the other beads will partially counteract the magnetic attraction, resulting in longer bead travel times (and larger fluctuations), as can be inferred from Fig. 2. In this case the bead density is $\rho = 0.247 \mu\text{m}^{-1}$, and the two-dimensional density of beads surrounding the well is $\sim 10^{-3} \mu\text{m}^{-2}$ (not counting the particles in the well).

B. Jamming upon chain penetration

Upon reaching the particle chain covering the potential well, the adsorbed particles are not able to penetrate into the chain immediately if they are stopped by other particles in the chain, and must therefore wait for some time interval Δt prior to entering the chain. Naturally, this can happen at any particle density, but the probability of colliding with one or more particles in the chain increases with ρ . For a completely homogenous chain, where all the particles have the same interdistance, it is expected that the particles always must wait for some time if $\rho > 1/4a$ [15]. Figure 3 shows the time interval Δt as a function of the chain density ρ . It is expected to diverge at the close-packed condition $\rho_c = 1/2a$, which makes it reasonable to use a power law to describe the waiting time:

$$\Delta t = \tau \left(1 - \frac{\rho}{\rho_c}\right)^{-\gamma}. \quad (2)$$

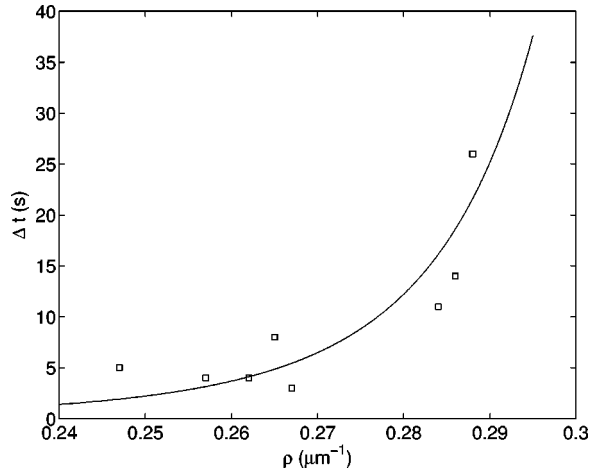


FIG. 3. The jamming time interval as a function of bead chain density. The solid line is a fit to the experimental data using Eq. (2).

Fitting Eq. (2) to the experiment, we find $\tau = 3.4$ ms and $\gamma = 5$. For higher loading of the well it becomes more and more difficult for additional beads to enter the chain giving rise to a jamming of particles that reach the loaded well, and the exponent γ is the measure of the “strength” of the divergency. However, we are not aware of any theory explaining the magnitude of our experimental value.

It is of interest to observe how much each bead is displaced upon penetration of an additional bead as a function of bead number N . Here $N=1$ corresponds to the beads closest to the penetrating bead, $N=2$ to the next nearest neighbors, and so on. Figure 4 shows the displacement Δu as a function of bead number at two different bead densities. The boxes correspond to $\rho = 0.262 \mu\text{m}^{-1}$, and the filled circles correspond to $\rho = 0.288 \mu\text{m}^{-1}$. It is clearly seen that more beads are influenced at higher densities. The displacement correlation length ξ is here defined as the length scale at which Δu drops to zero (i.e., below our spatial resolution limit), and is a measure of the number of beads that feel the

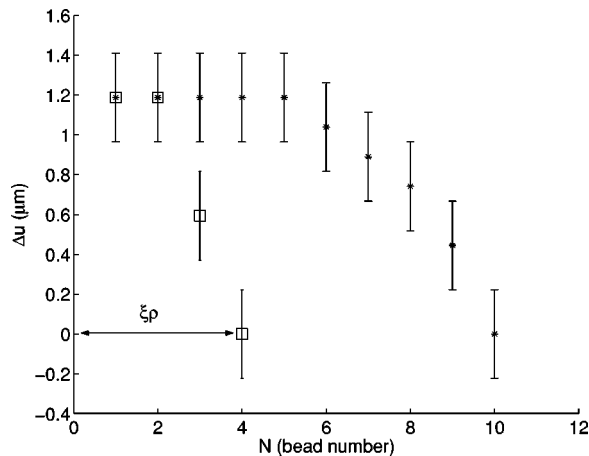


FIG. 4. The displacement of the beads upon penetration of an additional bead as a function of bead number for two different densities. Here the boxes correspond to $\rho = 0.262 \mu\text{m}^{-1}$, and the filled circles correspond to $\rho = 0.288 \mu\text{m}^{-1}$. The arrow shows the product $\xi\rho$ when $\rho = 0.262 \mu\text{m}^{-1}$.

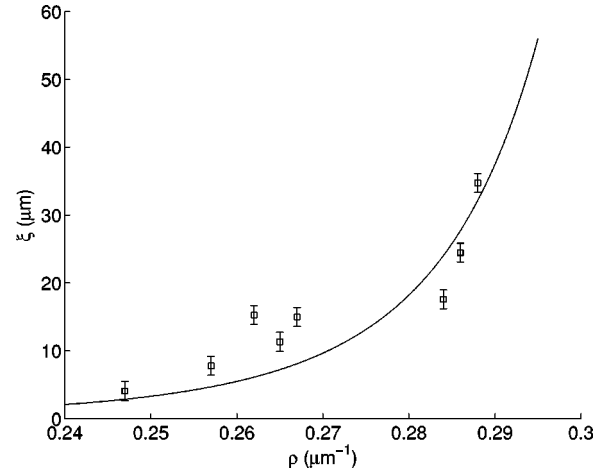


FIG. 5. The correlation length ξ as a function of bead chain density. The solid line is a fit to the experimental data using Eq. (3).

insertion of a new bead. Figure 5 shows the correlation length as a function of bead density. As with Δt , one may expect ξ to diverge at ρ_c , and we therefore tried to fit the experimental data using

$$\xi = \xi_0 \left(1 - \frac{\rho}{\rho_c} \right)^{-\gamma}. \quad (3)$$

The solid line in Fig. 5 shows the fit with $\xi_0 = 6 \times 10^{-3} \mu\text{m}$, and the same exponent as in Eq. (2). Equation (3) gives an alternative explanation why the waiting time in Eq. (2) is diverging. More and more particles in the chain are involved in a rearrangement upon penetration as one increases ρ . At ρ_c , all particles in the chain have to move in order to create a vacancy for the additional particle, and this process requires a considerable amount of time.

IV. DIFFUSION

When the beads enter the potential well minimum they are seen to diffuse along its length (i.e., in the y direction). In the case of a diluted bead mixture, we may load only a few beads into the potential well, thus allowing a study of the short time diffusion. Figure 6 shows six beads loaded into the well, whereas Fig. 7 shows how their position y varies with time, and these data can be used to evaluate the diffusion behavior. To this end, Fig. 8 shows the mean square displacement (MSD) $\langle (\Delta y)^2 \rangle$ along the chain as a function of time over a time interval of 100 s, measured at time steps of 1 s. The MSD was found by averaging over all the particles in the well. It is seen that the experimental data can be fit by a linear relationship,

$$\langle (\Delta y)^2 \rangle = 2Dt, \quad D = 0.11 \pm 0.01 \mu\text{m}^2 \text{ s}^{-1}. \quad (4)$$

This observation suggests that normal diffusion is important for the short time dynamics, in agreement with previous studies [10]. At later times one may expect a crossover to anomalous diffusion, but this is outside the scope of the present work.

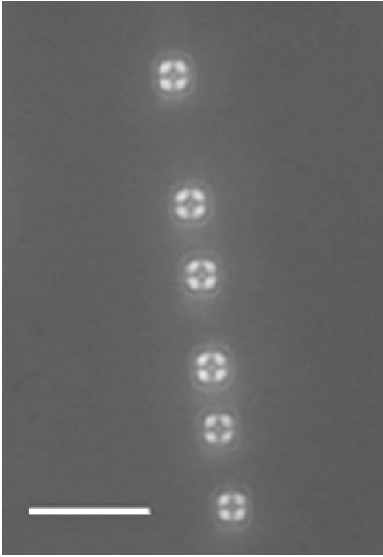


FIG. 6. A potential well with six beads used for observation of diffusion. The scalebar is $15 \mu\text{m}$.

The diffusion coefficient is related to the hydrodynamic drag coefficient through Einstein's relationship, $D = kT/f\eta a$, which allows us to estimate the hydrodynamic drag coefficient to be $f \approx 30$. This is a realistic value under the current circumstances. To this end, in the creeping motion approximation one finds that the drag coefficient is $f \approx -6\pi \ln(z/a-1)$ for a freely rotating sphere near the wall, whereas one has $f = 6\pi$ in the bulk [4]. Using the experimental value of f , we estimate the height to be $z \approx 1.7 \mu\text{m}$. On the other hand, an independent estimate based on the value of B found by fitting Eq. (1) to the experimental data gives $f \approx 10^3$, which is too high. This suggests that the value of the domain wall width assumed here is too large, since all other parameters are well known; that is, during the adsorp-

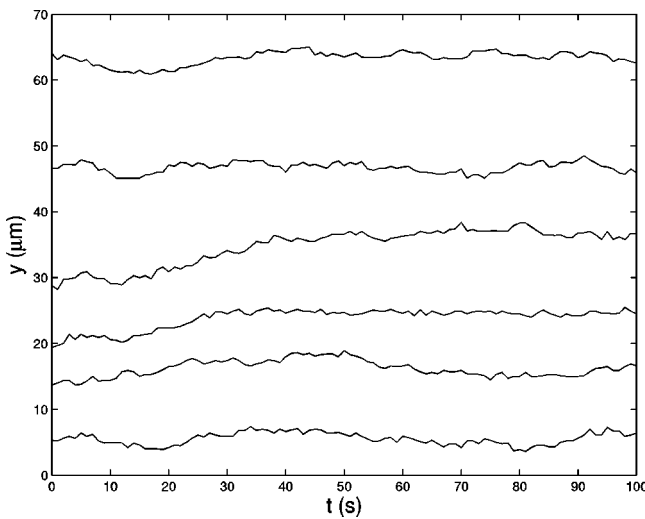


FIG. 7. The position y along the chain as a function of time for the six beads seen in Fig. 4. Here y is measured relative to a reference point on the frame. The chain bead density is $0.096 \mu\text{m}^{-1}$, and the six beads of the figure were the only ones in the field of view during the experiment.

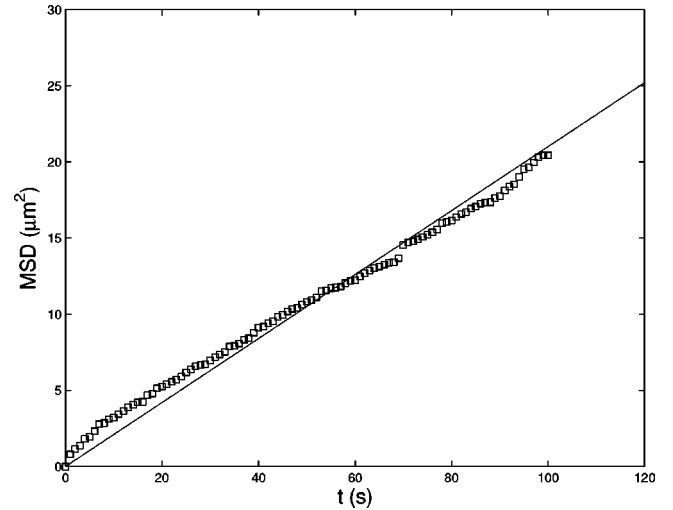


FIG. 8. The MSD as a function of time for the six beads seen in Fig. 4. The chain bead density is $0.096 \mu\text{m}^{-1}$. The solid line shows the best linear fit with $D = 0.11 \pm 0.01 \mu\text{m}^2 \text{s}^{-1}$.

tion process the particles interact with a domain wall of effective width $w_e \approx 50 \text{ nm}$, not the expected width $w \approx 300 \text{ nm}$. One could also imagine that the polyelectrolyte coating resists fast directed motion of the sphere (as opposed to diffusion). However, the origin of such a mechanism is not clear to us.

In the presence of the magnetic field from the domain wall, the magnetic interaction potential between two particles separated a distance d is

$$E(d) = \frac{\mu m^2}{4\pi d^3}, \quad m = \frac{4\pi}{3} a^3 \chi H_W, \quad (5)$$

where H_W is the field from the domain wall. It should be pointed out that this field is strongly inhomogeneous, which, in general, leads to complicated field distributions. Here we only wish to give some simple upper bound estimates, and therefore treat it as homogeneous with width $w \approx 300 \text{ nm}$. Then the domain wall aligns the particles with a field $H_W \sim M_s w / 2\pi a$. The interaction potential between two particles is $\sim kT$ when $d \sim 10a$, but increases with decreasing d . Thus, it is clear that the thermal fluctuations play an important role when the distance between the particles is large. It should also be pointed out that the electrostatic repulsion due to the surface charges of the beads play a role. In absence of any magnetic field we observe that the beads occasionally collide with each other, suggesting that the electrostatic interactions are comparable with the thermal energy. This means that when the particles are far from each other, we have seen that the short time behavior is governed by normal Fickian diffusion. On the other hand, when they are closer together one expects both the electric and magnetic interactions to be important, but this is outside the scope of the present study.

The depth of the well is estimated to be $\sim 10^4 kT$, using $E = -\mu_0 m H_W$. However, since the beads are much larger than the width of the domain wall, we expect the actual value to be smaller. In our experiments we observe some fluctua-

tions perpendicular to the potential well minimum (i.e., in the x direction), but they are, in general, much less than the particle radius. Moreover, we never observed any detachment from the potential well minimum, which suggests that the potential well is rather strong.

V. CONCLUSION

We have demonstrated a method for direct observation of adsorption and diffusion in a one-dimensional potential well. We found that the adsorption strongly depends on the bead density in the well, and that at the close-packed density the time it takes to penetrate into the bead chain diverges. We also found that at low bead densities in the well, the short time behavior is governed by normal diffusion. In our experiments, the external field was always kept zero, thus rendering the potential well and particle interactions the same. However, as was shown in Ref. [12], one may easily tune

these parameters using an external field. Moreover, it should also be possible to alter the potential well width by tuning the materials parameters of the magnetic film and thereby enabling control of the adsorption and diffusion. It should be pointed out that a domain wall is not required for the class of experiments reported here, and that similar experiments can be done by using prefabricated micro or nanomagnets (e.g., magnetic data tracks). However, in this case one loses the possibility to move the micromagnet to the wanted position, which may be advantageous in some cases.

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