Diffusion of Gold Nanorods on Chemically Functionalized Surfaces

By Sarah K. St. Angelo, Chad C. Waraksa, and Thomas E. Mallouk

The dynamical properties of spherical objects, such as random coil polymers, proteins, and colloidal particles, are well understood and have been studied by a variety of experimental techniques. Spheres in the sub-micrometer and micrometer size range have the attractive feature of allowing one to visualize crystallization, melting, and other processes that are difficult to observe directly with smaller objects.

Studies of this type have not yet been conducted with non-spherical particles, despite the fact that many interesting nanoscale objects such as bacteriophage viruses, nanowires, and nanotubes have high aspect ratios. The assembly of nanowires and nanotubes on surfaces is often accomplished by using chemical or fluidic methods. Therefore, understanding the dynamical properties of suspensions of high aspect ratio particles in contact with surfaces is an important step towards realizing self-assembling circuits, nanoscale machines, and other functional assemblies. Further, there is a wealth of theoretical work that motivates experimental studies of the dynamics and collective behavior of rod-like particles. We report here the visualization of two-dimensionally (2D) confined suspensions of metal nanorods, and determine their diffusion coefficients by particle tracking measurements. We find that the diffusion coefficient is strongly affected by the surface chemistry of the nanowires and the substrates, and by the dimensions of the nanowires themselves.

Diffusion coefficients may be obtained from observations of either ensemble or trajectory diffusion. Ensemble diffusion is usually measured when individual particles are not observable (e.g., molecules in solution) by spectroscopic or electrochemical techniques. Trajectory diffusion is commonly associated with the Brownian motion of large particles and may be observed directly by microscopy. Ensemble and trajectory diffusion experiments should yield the same results with the diffusion coefficient, \( D \), defined in the one-dimensional (1D) case as

\[
D = \frac{\langle x^2 \rangle}{2t}
\]

where \( \langle x^2 \rangle \) is the average of the square of the displacement and \( t \) is the time spanned by each displacement measurement. By measuring many values of particle displacement at regular time intervals we were able to calculate the diffusion coefficients for different sizes of particles on surfaces and were able to modulate \( D \) by altering the surface chemistry of the particles and the surfaces.

Gold nanorods were made by an electrochemical technique described previously. Aqueous suspensions of rods were diluted to a concentration of approximately \( 10^7 \) rods mL\(^{-1}\), and 10 \( \mu \)L was applied to a microscope slide. This provided sufficiently few rods that diffusion lengths were small compared to the average interparticle spacing. A spacer (120 \( \mu \)m thick) was used to seal the droplet under a transparent cover glass. The rods, which sank quickly to the surface of the microscope slide, were observed in the brightfield mode of Olympus BX60M metallurgical optical microscope.

We used a simple particle tracking technique based on color-coding of sequentially acquired video images. Particle images were converted to grayscale and then re-colored cyan, magenta, or yellow (CMY) in groups of three frames. Adjacent frames in the series were then superimposed. Particles that move appear as one of the three colors in the CMY composite image. Secondary colors appear when positional overlap of the particles occurs over two time periods, and black appears when there is positional overlap over three time periods, i.e., for particles that do not move on the timescale of sequential frames. For example, Figure 1a shows a brightfield image of 300 nm (diameter) \( \times 6 \mu \)m (length) Au rods derivatized with 2-mercaptoethanesulfonic acid (MESA) on a MESA-derivatized Au substrate. Figure 1b is the CMY composite image of Figure 1a and two subsequent images taken at 15 s intervals. Note that all MESA-coated particles (including

![Fig. 1. Optical micrographs of MESA-coated nanorods (300 nm \( \times 6 \mu \)m) on a MESA-coated substrate. a) Brightfield image. b) CMY composite image. Sequential images (cyan, magenta, yellow) are video frames at 15 s intervals. Circles show aggregates of nanowires which diffuse together.](image-url)
some that are aggregates of two rods) are mobile on this time-scale.

Individual particle trajectories were analyzed by measuring center-to-center displacements between sequential frames. Figure 2a shows a plot of 526 such displacements (each recorded after 10 s) for 300 nm × 6 μm MESA-coated rods on a MESA-covered surface. A small average displacement (black square) relative to the origin (cross) gives the drift of the particle ensemble over 10 s. This drift is likely due to the influence of gravity on the particles, since the microscope stage is not perfectly level. After subtracting the average drift from the displacements, the histogram of one-dimensional displacements (in the x- and y-directions) shown in Figure 2b was obtained. The data fit well to a Gaussian distribution, and a diffusion coefficient of 0.192 μm² s⁻¹ can be calculated from Equation 1. In this case, the diffusion length (2D²)¹⁄₂ is much smaller than the average interparticle spacing, and therefore a Gaussian distribution is expected.

Values of surface diffusion coefficients (D) obtained for different rod lengths (l), diameters (d), and monolayer coatings are given in Table 1. First, considering rods derivatized with MESA diffusing on a MESA-coated surface (anionic–anionic interaction), there is a stronger dependence of the diffusion coefficient on the length of the rod than on the diameter. For spherical colloids in solution, the diffusion coefficient is expected to vary inversely with the cube root of the volume. For high aspect ratio prolate ellipsoids, Stokes–Einstein theory predicts that the diffusion coefficient should scale as l⁻¹⁻³ d⁻²⁻³. For 2 and 6 μm long rods (d = 300 nm), the expected ratio of diffusion coefficients is 1.4, which is significantly less than that observed (2.2). Likewise, for d = 90 and 300 nm (l = 6 μm) a ratio of 2.1 is predicted, and 1.8 is observed. Hydrodynamic coupling of a particle to a surface is expected to reduce the diffusion coefficient, but again the effect of increasing length should be less than that of increasing diameter. We suspect that frictional interaction with the surface, which should have a stronger dependence on length than diameter, is the cause of the deviation from simple Stokes–Einstein behavior. Thus we can regard the particles as diffusing through a 2D fluid, but with some frictional interaction with the surface.

Table 1. Surface diffusion constants for several rod–surface combinations.

<table>
<thead>
<tr>
<th>Diameter × Length</th>
<th>Interaction</th>
<th>Diffusion coefficient, D [μm² s⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>A 300 nm × 6 μm MESA</td>
<td>anionic/anionic</td>
<td>0.19 ± 0.01</td>
</tr>
<tr>
<td>B 300 nm × 2 μm MESA</td>
<td>anionic/anionic</td>
<td>0.41 ± 0.13</td>
</tr>
<tr>
<td>C 90 nm × 6 μm MESA</td>
<td>anionic/anionic</td>
<td>0.34 ± 0.06</td>
</tr>
<tr>
<td>D 300 nm × 6 μm MESA</td>
<td>anionic/neutral</td>
<td>0.16 ± 0.01</td>
</tr>
<tr>
<td>E 300 nm × 2 μm MESA</td>
<td>anionic/neutral</td>
<td>0.44 ± 0.09</td>
</tr>
<tr>
<td>F 90 nm × 6 μm MESA</td>
<td>anionic/neutral</td>
<td>0.00</td>
</tr>
<tr>
<td>G 300 nm × 6 MESA</td>
<td>anionic/cationic</td>
<td>0.00</td>
</tr>
<tr>
<td>H 300 nm × 6 MESA</td>
<td>anionic/neutral</td>
<td>0.14 ± 0.06</td>
</tr>
<tr>
<td>I 300 nm × 6 MESA</td>
<td>anionic/neutral</td>
<td>0.16 ± 0.01</td>
</tr>
</tbody>
</table>

In order to study the effect of surface charge and hydrophilicity on diffusion, several different substrates (covered by neutral and cationic self-assembled monolayers (SAMs)) were also prepared. The interactions of anionic MESA-coated rods (300 nm × 6 μm) with the electro-neutral C₆₃H₃₃SH surface (Table 1, D) and with the deprotonated 2-mercaptoethylamine (MEA) surface (Table 1, H and I) gave D values that were similar to those found with the electrostatically repulsive MESA–MESA interaction (0.16, 0.14, 0.16 μm² s⁻¹, respectively). The similarity of these values again supports the idea that the rod and surface are weakly interacting, but that the friction is greater for less repulsive interactions. In contrast, the electrostatically attractive combination, MESA rods on an acid-rinsed MEA surface, showed no detectable diffusion.
over timescales of hundreds of seconds (0.00 μm²/s²). It is interesting that in the neutral MEA experiment, in which some of the surface amine groups are protonated, the diffusion coefficient was slightly lower than in the other cases.

A surprising result was obtained when measuring the diffusion coefficients of the three sizes of MESA particles on the neutral surface derivatized with hexadecanethiol (C₁₆H₃₃SH). Comparing D values to those found on the MESA surface, we found near agreement for all but the small-diameter particles (6 μm × 90 nm), which reproducibly stuck to the substrate immediately on contact. For larger particles, the long-range electrostatic force (presumably between the negatively charged sulfonate groups and an image charge in the substrate) is expected to dominate,[2] but for smaller ones the short-range van der Waals force is more important. Apparently, the two are closely balanced for the C₁₆H₃₃SH functionalized surface with rods of the size investigated here.

While the scaling of these interactions is not completely understood at present, these initial studies provide some guidance as to the conditions that are desirable for nanorod assembly experiments. The observation of pH-dependent diffusion may, for example, be useful for affixing particles to specific areas or in specific conformations on basic surfaces. More importantly, the particle tracking method described here provides a simple and convenient method for quantifying the surface diffusion of non-spherical particles under arbitrary conditions.

Experimental

Whatman Al₂O₃ filter membranes that contain 300–500 nm diameter internal pores were used as a template material. For 90 nm internal pore diameter, Al₂O₃ membranes were prepared in-house by the electrochemical anodization of an Al plate.[23] In both cases, one face of the membranes was coated with approximately 150 nm of thermally evaporated Ag. More Ag was electrodeposited (Silver 1024, Technic, Inc.) directly onto the evaporated Ag in order to close any open pores. This Ag layer was then used as the back contact in the electrochemical cell, and more Ag was deposited, further filling-in the pores. The membrane and cell were rinsed with deionized H₂O, and Au solution was added (Orotemp, Technic, Inc.). Plating was stopped with the desired rod length was reached. The Ag backing was removed by dissolving in 2 mL of 50 % HNO₃, and the Al₂O₃ template was dissolved in 2 mL of 5 M NaOH. The rods were sedimented using a laboratory centrifuge. The supernatant was removed and water was added. The rods were resuspended by physical agitation and brief immersion in an ultrasonic water bath. This rinsing process was repeated a total of five times in order to prepare the rods for addition of self-assembled monolayers (SAMs). Rods were derivatized with 2-mercaptoethanesulfonic acid, sodium salt (MESA, Aldrich) by suspending them in 1 mL of 1 mM MESA(aq) for 1 h. The MESA rods were then rinsed as described above, suspended in a total volume of 1 mL, and dialyzed 1,000-fold for imaging.

Microscope slides coated with 5 nm Cr/100 nm Au (EMF) were used as derivatizable surfaces in these experiments. Prior to derivatization, surfaces were cleaned with piranha solution (3:1 conc. H₂SO₄/30 % H₂O₂). After copious rinsing with water, the Au-coated slides were placed in 10 mM MESO(aq), 2-mercaptobenzylamine (MEA, Aldrich) (aq), or hexadecanethiol (Avocado Research Chemicals, Ltd.) (ethanol) for 1 h. The slides were rinsed with water, in the cases of MESO and MEA, or ethanol, in the case of hexadecanethiol. The surfaces were then dried under a stream of Ar. MEA slides were further treated with acidic or basic solutions in order to effect the protonation of the amino groups. Each MEA surface was rinsed with 0.01 M HCl(aq), 0.01 M NaOH(aq), or water, and immediately dried under Ar. The solutions were of pH 2.9, pH 12.6, and pH 8.5, respectively.

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Morphogenesis of One-Dimensional ZnO Nano- and Microrystals**

By Haoquan Yan, Rongrui He, Johnny Pham, and Peidong Yang*

During the past few years, much effort has been invested in controlling the sizes and shapes of inorganic nanocrystals, because these parameters represent key elements that determine their electrical and optical properties.[1-3] One way to achieve shape control is to enhance anisotropic nanocrystal growth using a liquid medium. The vapor–liquid–solid (VLS) growth mechanism, in which the nanowires grow out of supersaturated liquid alloy droplets, has been extremely successful in creating one-dimensional nanomaterials.[1-3] Another common approach is to use surfactants, regular or inverse micelles

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