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Hopping Diffusion of Gold Nanoparticles Observed with Liquid Cell TEM

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The diffusion of nanoparticles in the microfluidic cells used for liquid cell transmission electron microscopy (TEM) have always been found to be much slower [1-6], often by several orders of magnitude, when compared with bulk diffusion. While this highly suppressed motion is serendipitous for the atomic resolution imaging of nanoparticle nucleation and coalescence events, we still lack a compelling explanation for this anomalous phenomena. Here, we report results from our experiments tracking the motion of Au nanoparticles in water, using a combination of energy filtered imaging and image acquisition at frame rates of 100 Hz.

The Au nanoparticles (~20-70 nm in diameter) are dispersed in water and sandwiched between 30 nm thick SiN_x windows in a Hummingbird Scientific liquid flow holder. The holder is loaded into a JEOL 2200FS TEM with an Omega filter, where zero loss imaging (using a 20 eV energy slit) was used to mitigate the resolution loss from imaging through the liquid layer. Movies are recorded on a Direct Electron DE-12 camera system at 100 frames per second. The field of view is 819.2 nm by 819.2 nm and electron dose rate used was between 30-100 electrons/$Å^2$/s. The field of view and frame rate were chosen so that it was possible, in principle, to capture nanoparticles moving at bulk velocities, while minimizing the electron dose rate. The liquid layer thickness in each liquid cell was also measured using electron energy loss spectroscopy.

In these experiments, we observed that nanoparticles moved via surface hops. This motion is illustrated in Figure 1 as an image sequence where the nanoparticle made a series of such transient displacements over 0.10 seconds; 1 between the second and third frame, and at least 8 between the fourth and tenth frame, as inferred from the remnant contrast of the nanoparticle. We further deduce from the discontinuous motion blur that these displacements are discrete. The nanoparticle also appear to re-visit a few of the same locations. Figure 2 shows the entire recorded trajectory and the displacements between frames as a function of time. In general, the nanoparticles move in a pattern where intermittent hops that are tens of nanometers long are interspaced between lengthier segments of short displacements that are only a few nanometers long. Our analysis indicates that the short, stuck motion is similar to the reported suppressed diffusion, whereas during hops, the nanoparticles have mobility only two to three orders of magnitude slower than bulk values calculated from the Stokes-Einstein equation. We propose that the observed motion is due to surface potential wells, where a nanoparticle can make larger displacements when it escapes a trapping well. This motion is, however, short-lived because the nanoparticle is quickly trapped again. The implications of this study will be discussed. [7]

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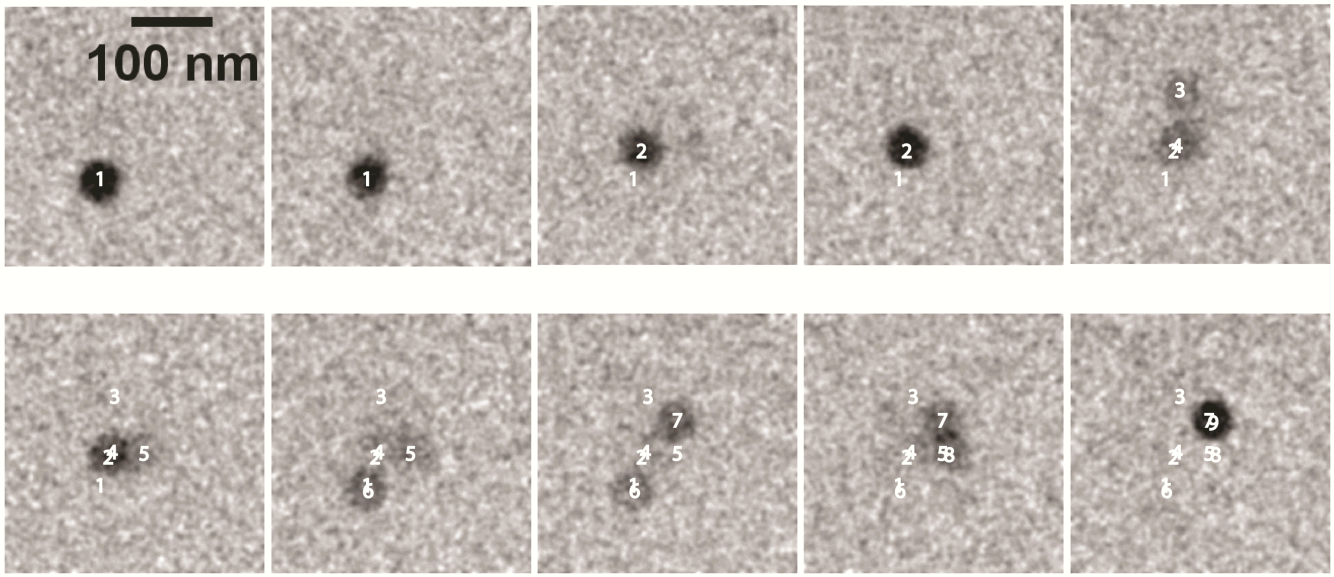

Figure 1. A 0.10 second image sequence illustrating the hopping motion (each frame is 10 ms long). The electron dose rate is 100 $e^-/Å^2/s$. Liquid layer thickness is measured to be ~70 nm from EELS. Discontinuous contrast in the motion blur indicates that the nanoparticle sticks for a short time before making the next hop. Nanoparticle positions that can be resolved are denoted by running numbers.

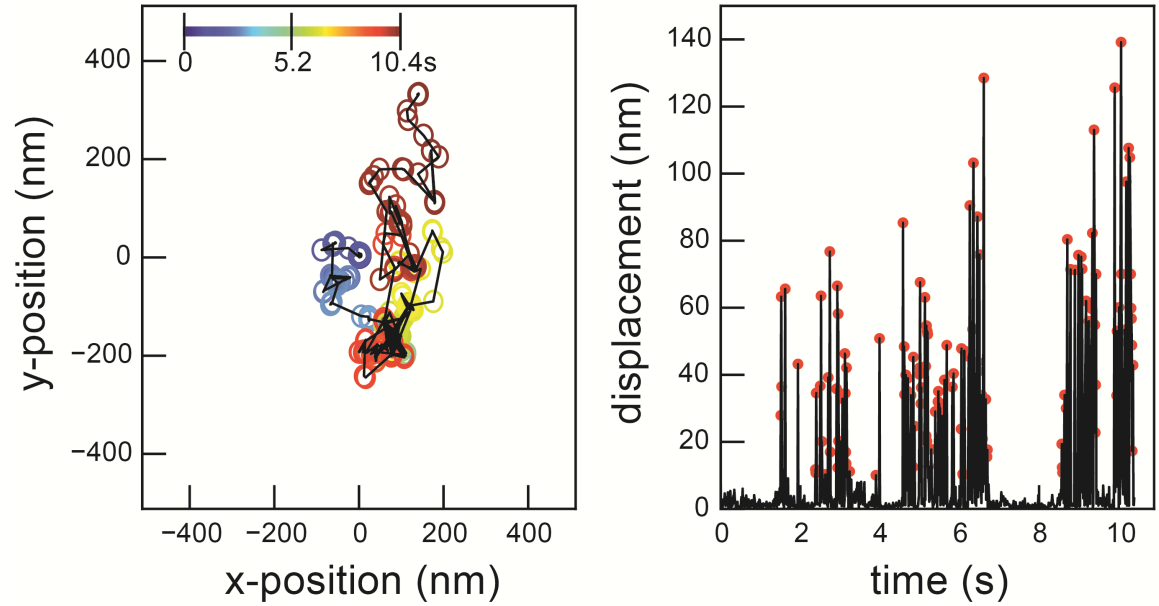

Figure 2. (Left) The full 10 second nanoparticle trajectory where the particle position versus time is denoted using empty colored circles. (Right) Displacement between frames plotted as a function of time. Displacements longer than 10 nm are denoted with red circles.

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