Gold nanoparticles: enhanced optical trapping and sensitivity coupled with significant heating

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Gold nanoparticles appear to be superior handles in optical trapping assays. We demonstrate that relatively large gold particles ($R_b=50$ nm) indeed yield a sixfold enhancement in trapping efficiency and detection sensitivity as compared to similar-sized polystyrene particles. However, optical absorption by gold at the most common trapping wavelength (1064 nm) induces dramatic heating ($266^\circ$C/W). We determined this heating by comparing trap stiffness from three different methods in conjunction with detailed modeling. Due to this heating, gold nanoparticles are not useful for temperature-sensitive optical-trapping experiments, but may serve as local molecular heaters. Also, such particles, with their increased detection sensitivity, make excellent probes for certain zero-force biophysical assays. © 2006 Optical Society of America

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Gold nanoparticles have found broad applications in nanomaterials and nanobiotechnology. In optical trapping studies, gold nanoparticles have been investigated as superior handles relative to polystyrene (PS) beads because gold’s high polarizability could lead to higher trap efficiency. Such a large polarizability also offers the crucial added benefit of enhanced detection.

In 1994, Svoboda and Block demonstrated optical trapping of small metallic particles by using 18 nm enhanced detection. In this Letter, we report a combined experimental and theoretical study of laser-induced heating of optically trapped gold nanoparticles. Specifically, we demonstrate that large gold beads ($R_b=50$ nm), referred to similar-sized PS beads, have a sixfold enhancement in both $k_{\text{trap}}$ and detector sensitivity. However, we also found dramatic heating of 266° C/W. By using a small laser power (<1 mW) to avoid this heating, gold’s enhanced sensitivity led to improved bandwidth and reduced entropic repulsion in certain zero-force biophysical assays.

Our optical trapping instrument used a 1064 nm laser for trapping and 810 and 850 nm diode lasers for position detection, similar to earlier work. Measurements were taken in a buffered aqueous solution 830 nm from the surface by using an estimated laser power at the focus, $P$. As a control, we measured $k_{\text{trap}}$ for ten PS beads ($R_b=200$ nm) by three different methods at five laser powers and found agreement within 7% (data not shown).

For our experimental investigation of temperature-induced heating, we employed three methods for estimating $k_{\text{trap}}$: equipartition theorem ($k_{\text{eq}}$), power spectrum ($k_{ps}$), and hydrodynamic drag ($k_d$). Each method depends on different physical parameters and assumptions. A robust measurement of $k_{\text{trap}}$ is achieved only if all three methods agree. Focusing on the temperature ($T$) dependence, we note that $k_{\text{eq}}$ depends linearly on $T$ ($k_{\text{eq}}=k_B T/(\pi x^2)$, where $x$ is the bead’s position). Neither $k_{ps}$ nor $k_d$ explicitly depends on $T$; rather they depend linearly on the fluid viscosity ($\eta$) where $k_{ps}=12\pi R_b^2 \eta f_0^2$ with $f_0$ as the modified Lorenzian roll-off frequency and $k_d=6\pi R_b \eta v/x$ with $v$ as the fluid velocity. Water’s viscosity decreases as $T$ increases.

Two experimental signatures can indicate significant heating: (i) superlinear scaling of $k_d$ and $k_{ps}$ with $P$, and (ii) diverging estimations of $k_d$ or $k_{ps}$ from $k_{eq}$ with increasing $P$. Both effects arise from an
unaccounted-for $T$ increase with an accompanying decrease in $\eta$.

The initial motivation for trapping gold particles was their potentially enhanced $k_{\text{trap}}$. This enhancement for large particles has not been quantified. At a moderate power ($P=205$ mW), we compared gold ($R_b=50$ nm) to PS beads ($R_b=55$ nm) [Figs. 1(a) and 1(b)]. We found for gold (versus PS) $k_{\text{eq}}=12$ (versus 2.2) fN/nm and $k_{\text{ps}}=25$ (versus 2.5) fN/nm. Thus there was a substantial enhancement, yet the large disagreement between $k_{\text{eq}}$ and $k_{\text{ps}}$ suggested significant heating.

To investigate this putative heating, we determined $k_{\text{ps}}, k_{\text{eq}},$ and $k_d$ for ten individual gold particles ($R_b=50$ nm) at five different power levels. Trap linearity, a crucial assumption in the power spectrum and equipartition calibrations, was excellent as verified by hydrodynamic drag calibration [Fig. 1(c)]. We found that averages of $k_d$ and $k_{\text{ps}}$ had a superlinear dependence on $P$ and diverged from the average $k_{\text{eq}}$ as $P$ increased [Fig. 1(d)]. One might argue that $k_d$ should be less affected by local heating than $k_{\text{ps}}$, since water is being moved rapidly around the trapped particle, potentially cooling it. However, we found that $k_d$ and $k_{\text{ps}}$ agree; this agreement arises because the thermal equilibration time ($3.6$ ns for $R_b=50$ nm) (Ref. 8) is $10^5$ times faster than the fluid traverses the bead’s diameter at $v=200 \mu\text{m/s}$. In summary, at the minimum $P$ necessary to trap these large gold beads, we had agreement between all three calibration methods. Yet, as $P$ increased, there was a rapid divergence in estimations of $k_{\text{trap}}$.

To understand the origin of the heating, we modeled a trapped gold bead absorbing infrared light and conducting the resulting heat into the surrounding fluid. Under steady state conditions, the radial temperature profile around the particle is $T(r)=T_0 + P_{\text{abs}}/(4\pi\eta C)$, where $T_0$ is room temperature ($293.3$ K), $P_{\text{abs}}$, the absorbed power, is given by $P_{\text{abs}} = \sigma_{\text{abs}} I(z)^2$, $C$ is the conductivity of water (0.6 W/K m), and $r$ is the radial distance from the gold bead’s center. Radiation pressure leads to stable

Fig. 1. (a) Position record, $x$, of a gold (dark gray) and a polystyrene, PS (light gray), bead smoothed to 200 Hz. (b) Averaged power spectra fit for the same gold (dark gray) and PS bead (light gray). Modified Lorentzian (Ref. 6) fits (solid curve) yielded roll-off frequencies, $f_0$ of $4283.1 \pm 9.8$ Hz and $330.1 \pm 0.7$ Hz, respectively. Measurements were done using a gold ($R_b=50$ nm) and a PS ($R_b=55$ nm) particle at a 200 kHz data acquisition rate and $P=205$ mW. (c) Hydrodynamic drag calibration of a gold particle (circle) demonstrating trap linearity, where $k_d=23$ fN/nm was deduced by a linear fit (line). Inset: histogram of $x$ fitted to a Gaussian confirms trap linearity. (d) Comparison of the three different estimations of trap stiffness as a function of laser power, $k_d$ (circle), $k_{\text{eq}}$ (rectangle), and $k_{\text{ps}}$ (triangle).

Fig. 2. (a) Temperature gradient surrounding an optically trapped gold particle ($R_b=50$ nm) at $P=205$ mW. (b) Temperature (red) and water viscosity (blue) at the particle surface as a function of laser power. (c) Estimations of $k_{\text{trap}}$, using the data in Fig. 1(d), corrected for local temperature and viscosity with $k_d$ (circle), $k_{\text{eq}}$ (rectangle), and $k_{\text{ps}}$ (triangle).
trapping at a distance $z$ from the beam focus, so $I(z) = P/[\pi w^2(z)]$ with $w(z)$, the beam radius variation along the optical axis, given by $w(z) = w_0(1 + (z/z_0)^2)^{1/2}$. We determined the beam waist ($w_0 = 427$ nm) and the Rayleigh length ($z_0 = 606$ nm) based on Pralle et al.\cite{3} as well as $z = 200$ nm based on Neuman and Block.\cite{10} The absorption cross section of a Rayleigh particle is $\sigma_{abs} = 2 \pi n_m^{2}/\lambda \text{Im}[3V(\varepsilon_\infty - \varepsilon_0)]/(\varepsilon_\infty + 2\varepsilon_0)$. The electric permittivities of gold and water are $\varepsilon_\infty = -54 + i5.9$ and $\varepsilon_0 = 1.77$ at $\lambda = 1047$ nm.\cite{2} We also use the refractive index of water ($n_m = 1.33$), the trapping wavelength ($\lambda = 1064$ nm), and the gold bead’s effective volume ($V$) due to its skin depth.\cite{2} With no free parameters, we calculated $T$ at the surface of the particle and thereby deduced $T(r)$ and the corresponding $\eta$ at the bead–fluid interface [Figs. 2(a) and 2(b)]. Using this modeling, we calculated a dramatic heating ($\Delta T = 266^\circ C/W$).

Is this model correct? If so, we should attain a consistent estimate of $k_{trap}$ from $k_{ps}$ and $k_{eq}$ that removes the widening divergence shown in Fig. 1(d). Figure 2(c) shows the quantitative agreement between all three methods after the proper local $T$ and $\eta$ were included. We repeated the measurements and modeling with 40 nm radius gold particles, again achieving quantitative agreement (data not shown). Thus our results demonstrate substantial heating of trapped gold beads arising from gold’s absorption at 1064 nm.

We can take advantage of the gold beads’ enhanced sensitivity with single-molecule biophysics techniques that use low optical power ($\sim 1$ mW). For example, the tethered particle method (TPM) assay typically uses a medium-sized PS bead as a reporter for the end-to-end distance of DNA.\cite{11} Recent theoretical research points to a small, but important, effective entropic force present in these assays.\cite{12} To minimize this effect, smaller beads are better. Further, smaller beads have reduced hydrodynamic drag, enabling faster averaging of Brownian motion to reveal the underlying signal. However, smaller beads have decreased signal sensitivities, potentially decreasing spatial resolution.

We measured a sixfold higher sensitivity in back focal plane detection for gold versus similar-sized PS beads when using 810 nm light (data not shown). In TPM assays comparing gold beads ($R_b = 50$ nm) to PS beads ($R_b = 150$ nm) with comparable sensitivity, we measured a sixfold increase in time resolution [as deduced from the autocorrelation time when using a 250 nm DNA molecule (data not shown)] and calculated a threefold reduction in entropic repulsion. For laser-based bead tracking, smaller beads have the additional benefit of allowing longer DNA molecules within the limited detection range.

In conclusion, we have shown that gold beads are not good handles for applying forces to biological molecules. The measured heating of 266°C/W is $> 20$ times higher than the trapping laser-induced heating of water;\cite{13} such heating ($\Delta T = 55^\circ C$ even at low $k_{trap}$ [12 fN/nm]) could damage biomaterials such as enzymes. In certain applications, this dramatic heating could be exploited to locally unfold protein or RNA molecules. In addition, solid gold beads show significant advantages in zero-force application of TPM: increased sensitivity, increased temporal resolution, and reduced entropic repulsion. Further, we anticipate larger sensitivity enhancements for shorter wavelengths up to a gold particle’s plasmon resonance.

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References