

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

Yeonee Seol

JILA, University of Colorado, and National Institute of Standards and Technology, Boulder, Colorado 80309

Amanda E. Carpenter

JILA, University of Colorado, and National Institute of Standards and Technology, and Department of Physics, University of Colorado, Boulder, Colorado 80309

Thomas T. Perkins

JILA, University of Colorado, and National Institute of Standards and Technology, and Department of Molecular, Cellular and Developmental Biology, University of Colorado, Boulder, Colorado 80309

Received February 21, 2006; accepted May 10, 2006;
posted May 30, 2006 (Doc. ID 68322); published July 25, 2006

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°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

OCIS codes: 140.7010, 160.3900, 350.5340.

Gold nanoparticles have found broad applications in nanomaterials and nanobiotechnology.¹ 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.^{2,3} 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 radius (R_b) gold beads.² These beads had a sevenfold higher trap stiffness (k_{trap}) than similar-sized PS beads, but a scaling analysis suggested a rapid destabilization of trapping for larger particles. Thus it was noteworthy that stable trapping of gold beads over an expanded range ($9 \leq r \leq 125$ nm) was recently reported by Hansen *et al.*³ While these experiments used the minimum laser power necessary for stable trapping, the authors predicted a maximum force of 30 pN could be exerted at high laser power (~ 4.5 W).

Dramatic heating at such a laser power, potentially due to gold's nonnegligible absorption, could be a severe problem, causing damage to biological samples and, as we demonstrate, incorrect determination of k_{trap} . 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), referenced to similar-sized PS beads, have a sixfold enhancement in both k_{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.⁴ 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_{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_{trap} : equipartition theorem (k_{eq}), power spectrum (k_{ps}), and hydrodynamic drag (k_{d}). Each method depends on different physical parameters and assumptions. A robust measurement of k_{trap} is achieved only if all three methods agree.⁵ Focusing on the temperature (T) dependence, we note that k_{eq} depends linearly on T ($k_{\text{eq}}=k_{\text{B}}T/\langle x^2 \rangle$, 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 (η) where $k_{\text{ps}}=12\pi^2 R_b \eta f_0$ with f_0 as the modified Lorentzian roll-off frequency⁶ and $k_{\text{d}}=6\pi R_b \eta \nu/x$ with ν as the fluid velocity.⁵ Water's viscosity decreases as T increases.⁷

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

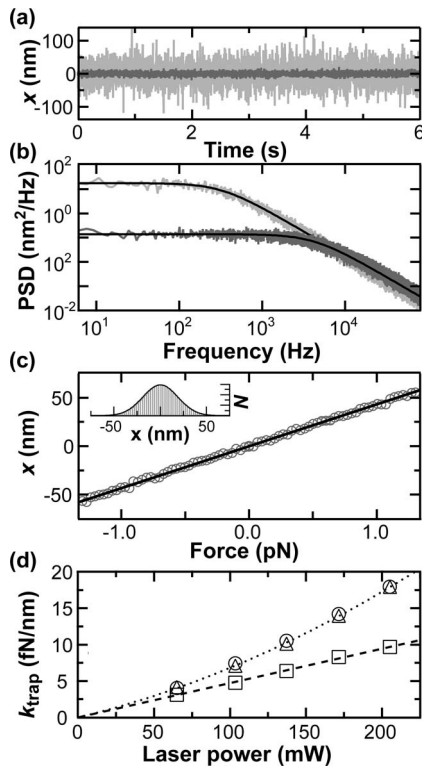


Fig. 1. (a) Position record, x , of a gold (dark gray) and a polystyrene, PS (light gray), bead smoothed to 200 Hz. (b) Averaged power spectra fit for the same gold (dark gray) and PS bead (light gray). Modified Lorentzian (Ref. 6) fits (solid curve) yielded roll-off frequencies, f_0 of 4283.1 ± 9.8 Hz and 330.1 ± 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 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_{eq} (rectangle), and k_{ps} (triangle).

unaccounted-for T increase with an accompanying decrease in η .

The initial motivation for trapping gold particles was their potentially enhanced k_{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) $k_{eq}=12$ (versus 2.2) fN/nm and $k_{ps}=25$ (versus 2.5) fN/nm. Thus there was a substantial enhancement, yet the large disagreement between k_{eq} and k_{ps} suggested significant heating.

To investigate this putative heating, we determined k_{ps} , k_{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,⁵ was excellent as verified by hydrodynamic drag calibration [Fig. 1(c)]. We found that averages of k_d and k_{ps} had a superlinear dependence on P and diverged from the average k_{eq} as P increased [Fig. 1(d)]. One might argue that k_d

should be less affected by local heating than k_{ps} , since water is being moved rapidly around the trapped particle, potentially cooling it. However, we found that k_d and k_{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_{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 $T(r)=T_\infty + P_{abs}/(4\pi rC)$, where T_∞ is room temperature (293.3 K), P_{abs} , the absorbed power, is given by $P_{abs} = \sigma_{abs} I(z)$,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

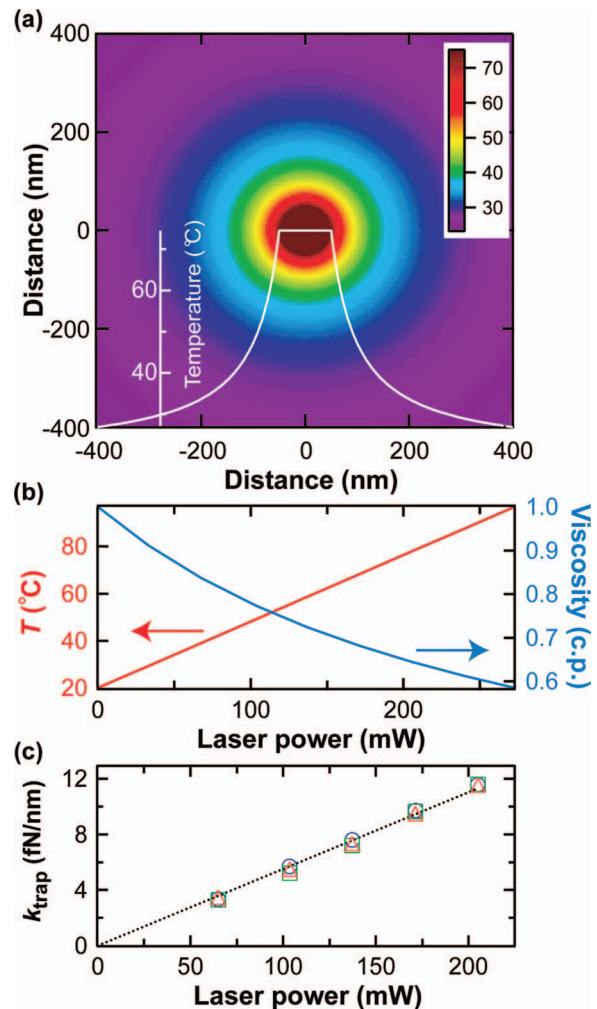


Fig. 2. (a) Temperature gradient surrounding an optically trapped gold particle ($R_b=50$ nm) at $P=205$ mW. (b) Temperature (red) and water viscosity (blue) at the particle surface as a function of laser power. (c) Estimations of k_{trap} , using the data in Fig. 1(d), corrected for local temperature and viscosity with k_d (circle), k_{eq} (rectangle), and k_{ps} (triangle).

trapping at a distance z from the beam focus, so $I(z) = P / [\pi w(z)^2]$ 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.*⁹ as well as z ($=200$ nm) based on Neuman and Block.¹⁰ The absorption cross section of a Rayleigh particle is $\sigma_{\text{abs}} = 2\pi m_m / \lambda \text{Im}[3V(\epsilon_g - \epsilon_w) / (\epsilon_g + 2\epsilon_w)]$. The electric permittivities of gold and water are $\epsilon_g = -54 + i5.9$ and $\epsilon_w = 1.77$ at $\lambda = 1047$ nm.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.² With no free parameters, we calculated T at the surface of the particle and thereby deduced $T(r)$ and the corresponding η at the bead–fluid interface [Figs. 2(a) and 2(b)]. Using this modeling, we calculated a dramatic heating ($\Delta T = 266^\circ\text{C/W}$).

Is this model correct? If so, we should attain a consistent estimate of k_{trap} from k_d , 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 η 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 (<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.¹¹ Recent theoretical research points to a small, but important, effective entropic force present in these assays.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 water¹³; such heating ($\Delta T = 55^\circ\text{C}$ 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.

T. T. Perkins acknowledges the support of a W. M. Keck grant in the RNA Sciences and a Burroughs Wellcome Fund Career Award in the Biomedical Sciences. A. E. Carpenter acknowledges support from NIH training grant T32 GM065103. This work was also supported by the National Science Foundation (Phy-0404286 and Phy-0096822) and NIST. T. T. Perkins is a staff member of NIST's Quantum Physics Division. His e-mail address is tperkins@jila.colorado.edu.

References

1. M. C. Daniel and D. Astruc, *Chem. Rev.* (Washington, D.C.) **104**, 293 (2004).
2. K. Svoboda and S. M. Block, *Opt. Lett.* **19**, 930 (1994).
3. P. M. Hansen, V. K. Bhatia, N. Harrit, and L. Oddershede, *Nano Lett.* **5**, 1937 (2005).
4. L. Nugent-Glandorf and T. T. Perkins, *Opt. Lett.* **29**, 2611 (2004).
5. K. Svoboda and S. M. Block, *Annu. Rev. Biophys. Biomol. Struct.* **23**, 247 (1994).
6. K. Berg-Sørensen and H. Flyvbjerg, *Rev. Sci. Instrum.* **75**, 594 (2004).
7. R. C. Weast, *CRC Handbook of Chemistry and Physics*, (CRC, 1984).
8. K. Pustovalov, *Int. J. Heat Mass Transfer* **36**, 391 (1993).
9. A. Pralle, M. Prummer, E.-L. Florin, E. H. K. Stelzer, and J. K. H. Horber, *Microsc. Res. Tech.* **44**, 378 (1999).
10. K. C. Neuman and S. M. Block, *Rev. Sci. Instrum.* **75**, 2787 (2004).
11. L. Finzi and J. Gelles, *Science* **267**, 378 (1995).
12. D. E. Segall, P. C. Nelson, and R. Phillips, *Phys. Rev. Lett.* **96**, 088306 (2006).
13. E. J. G. Peterman, F. Gittes, and C. F. Schmidt, *Biophys. J.* **84**, 1308 (2003).