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## Supporting Information:

“Photothermal Correlation Spectroscopy of Gold Nanoparticles in Solution”

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## A: Photothermal Signal-to-Noise ratio and numerical aperture

We assume a shot-noise-limited photothermal detection. The intensity of the probe beam in the focus ( $I_{probe}$ ) is

$$I_{probe} = \frac{P_{probe}}{A} \propto \frac{P_{probe}}{(\lambda / NA)^2}, \quad (A1)$$

and the magnitude of the reference field ( $E_{ref}$ ) in the focus is:

$$E_{ref} \propto NA \cdot \sqrt{P_{probe}}. \quad (A2)$$

The probe power collected by the objective lens at a distance  $r$  is defined by the reference field ( $e_{ref}$ ) within a solid angle defined by the  $NA$ :

$$P_{ref} = P_{probe} \propto \int r^2 d\Omega \cdot e_{ref}^2. \quad (A3)$$

This results in

$$e_{ref} \propto \frac{1}{r \cdot NA} \sqrt{P_{probe}} \quad (A4)$$

Away from the focus the scattered electric field ( $e_{sc}$ ) decreases inversely proportional to the distance  $r$  providing with the magnitude of the scattered field:

$$e_{sc} \sim \frac{1}{r} E_{ref} = \frac{1}{r} NA \cdot \sqrt{P_{probe}}. \quad (A5)$$

The photothermal signal is proportional to the product of the reference and scattered fields away from the focus integrated in a solid angle defined by  $NA$ :

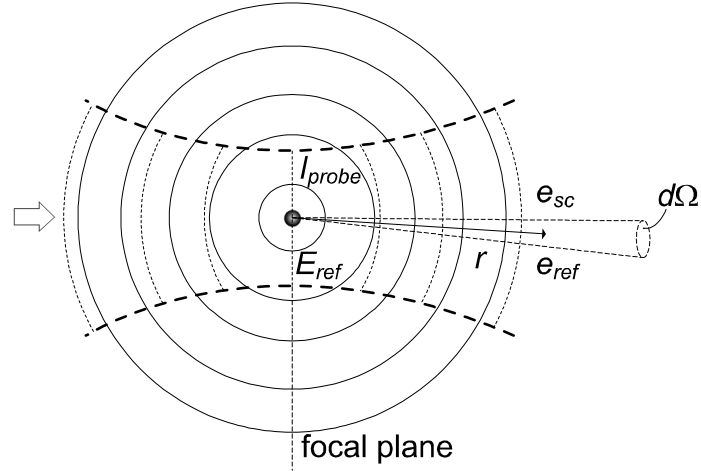
$$S \propto \int r^2 d\Omega \cdot e_{sc} \cdot e_{ref}. \quad (A6)$$

Taking into consideration  $e_{ref}$  and  $e_{sc}$ , the signal depends on  $NA$  in the following way:

$$S \propto NA^2 \cdot P_{probe}. \quad (A7)$$

The noise ( $N$ ) for photothermal detection is independent of  $NA$ , thus providing the signal-to-noise ratio ( $SNR$ ):

$$SNR \propto NA^2 \cdot \sqrt{P_{probe}}. \quad (A8)$$



**Figure A.** Schematic representation of the electric fields in photothermal detection. The surfaces of constant phase for spherical waves generated by the single nanoparticle (solid lines), and the Gaussian beam wavefront for the probe beam (dashed lines).  $I_{probe}$  is the intensity of the probe beam in the focus;  $E_{ref}$  and  $e_{ref}$  are magnitudes of the reference field in the near-field and far-field regions at the distance  $r$ , respectively; and  $e_{sc}$  is the scattered electric field in the far-field region;  $d\Omega$  is the elementary solid angle.

## B: Diffusion in water and water:glycerol mixtures and influence of the heating

The diffusion time of nanoparticles in the detection volume is given by the equation:

$$\tau_d = \frac{\omega_0^2}{4D}, \quad (\text{B1})$$

where  $D$  is the diffusion coefficient according to the Stokes-Einstein relation:

$$D = \frac{k_B T}{6\pi\eta R}. \quad (\text{B2})$$

The viscosity of the medium around nanoparticles is reduced because of the local heating. To account for this effect, we introduce an adjustable parameter,  $r_{av}$ , the radius over which we average the temperature increase  $\Delta T \approx 0.6 \frac{P_{abs}}{4\pi\kappa r_{av}}$ . The effective viscosity then becomes  $\eta = \eta(T_0 + \Delta T)$ , with  $T_0 = 295$  K. The viscosity therefore depends on the absorbed power  $P_{abs}$ , and the equation for the diffusion time becomes:

$$\tau_d = \frac{3}{2} \frac{\pi R \omega_0^2}{k_B} \frac{\eta \left( T_0 + 0.6 \frac{P_{abs}}{4\pi\kappa r_{av}} \right)}{T_0 + 0.6 \frac{P_{abs}}{4\pi\kappa r_{av}}}. \quad (\text{B3})$$

The dependence of the viscosity is different for pure water and water:glycerol mixtures (see Fig. B below).

In the case of water we assume that {Handbook of Chemistry and Physics; 72nd ed., CRC Press: Boca Raton, FL, 1991}:

$$\eta(T) = 1.7585 \cdot 10^{-6} \cdot e^{1870.3/T} \quad (\text{B4})$$

In the case of water:glycerol mixture the thermal properties of the medium and the viscosity will change. The heat capacity per unit volume of the mixture ( $C_p^{mix}$ ) and the thermal conductivity of the mixture ( $\kappa^{mix}$ ) can roughly be approximated by interpolating between the parameters for pure water and glycerol as follows:

$$C_p^{mix} = w^{water} C_p^{water} + w^{glycerol} C_p^{glycerol} \quad (\text{B5})$$

$$\kappa^{mix} = w^{water} \kappa^{water} + w^{glycerol} \kappa^{glycerol} \quad (\text{B6})$$

where  $w$  is the mass fraction of the mixture, thus giving  $C_p^{mix} = 3.24 \times 10^6 \text{ JK}^{-1}\text{m}^{-3}$  and  $\kappa^{mix} = 0.33 \text{ WK}^{-1}\text{m}^{-1}$ . The viscosity of the 1:1 mixture is estimated based on the method of Teja and Rice {Reid, Prausnitz and Poling, The Properties of Gases and Liquids, McGraw-Hill, 4ed.} as

$$\ln(\eta^{mix} \epsilon^{mix}) = x^{water} \ln(\eta^{water} \epsilon^{water}) + x^{glycerol} \ln(\eta^{glycerol} \epsilon^{glycerol}), \quad (\text{B7})$$

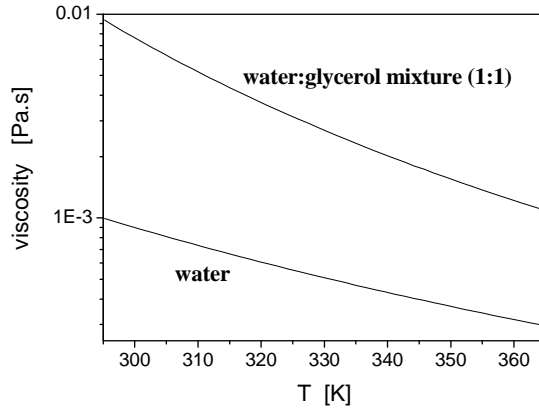
where

$$\epsilon = \frac{V_c^{2/3}}{(T_c M)^{1/2}} \quad (\text{B8})$$

with  $V_c$  and  $T_c$  being the critical volume and temperature, respectively, and  $M$  the molar mass. The viscosity of the glycerol is approximated by

$$\eta^{mix}(T) = A \cdot 10^{B/(T-T_l)}, \quad (\text{B9})$$

where  $A = 3.54 \times 10^{-6} \text{ Pa}\cdot\text{s}$ ,  $B = 780 \text{ K}$ ,  $T_l = 153 \text{ K}$ .



**Figure B.** Viscosity of water and calculated viscosity of a 1:1 water:glycerol mixture as functions of the temperature.