Temperature Measurements of a Single Gold Nanoparticle under Laser illumination

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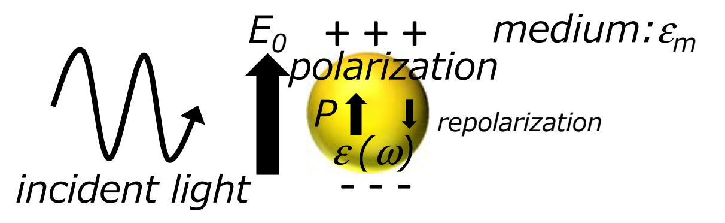
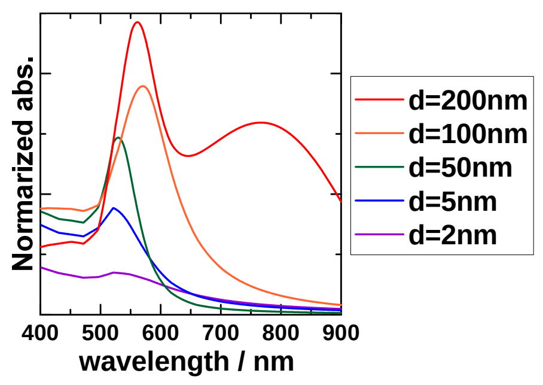
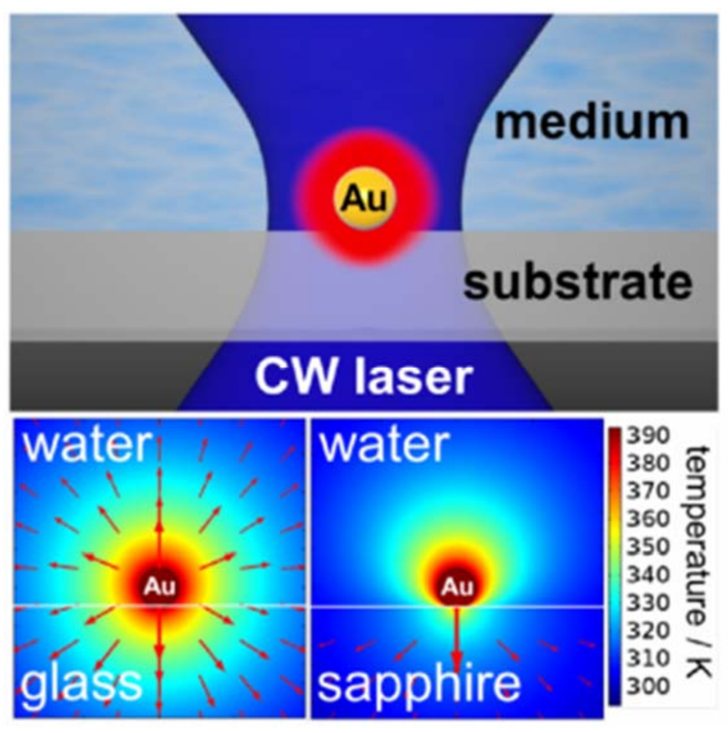
Introduction

Plasmonic nanoparticles (NPs) and nanostructures have attracted much attention because of enhanced electromagnetic field in the near-field regime generated by excitting the **surface plasmon resonance (SPR)** band.

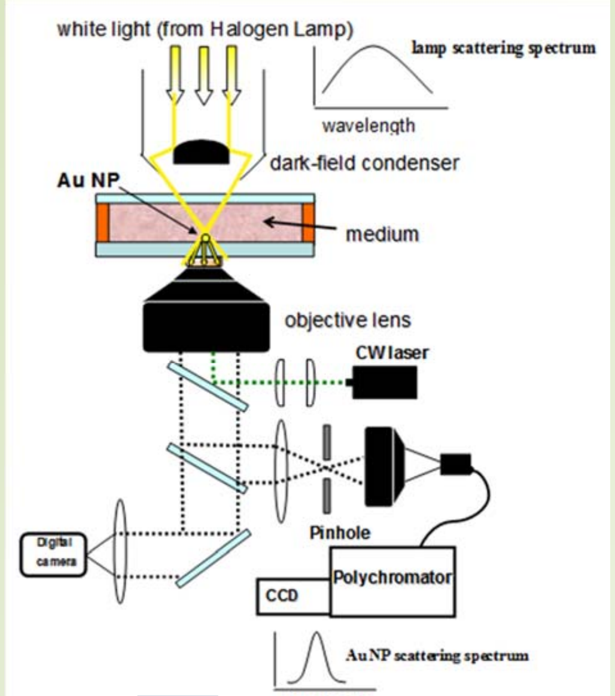


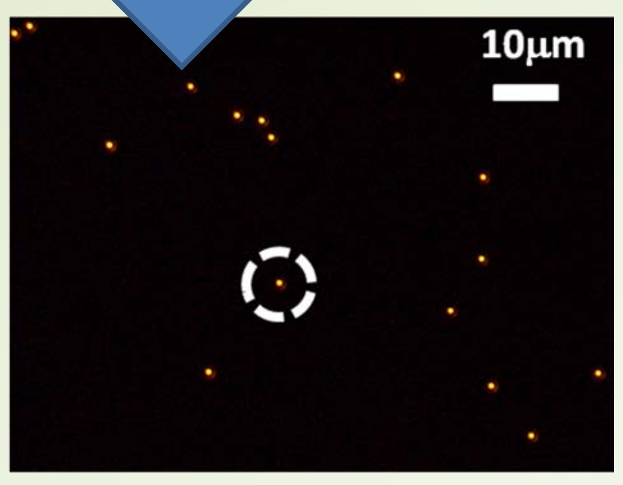


Temperature measurement of nanoparticles (NPs) due to heating by laser illumination is important for photothermal cancer therapy and nanofabrication. We implemented the method to estimate the local temperature of a laser-heated gold NP on glass substrate in various surrounding media by applying the light scattering spectroscopy. We discuss experimental results in comparison with the calculation by COMSOL. We found that the contact area of NP/substrate and co-adsorbed water layer on the substrate is crucial to the computational resuts.

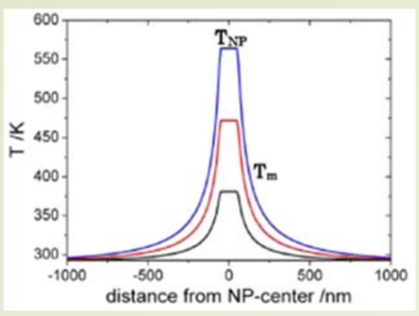


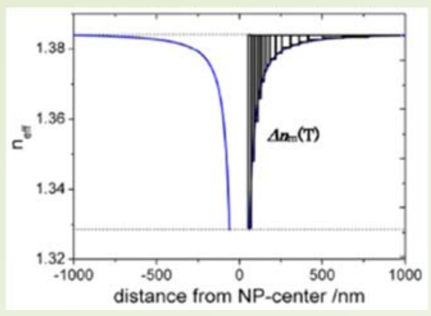
Experimental

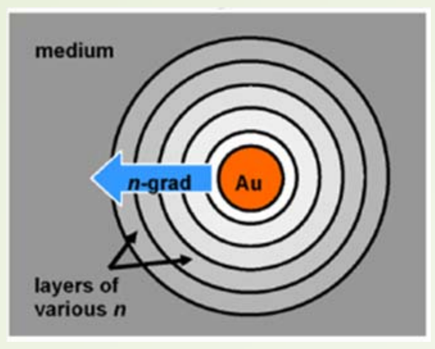




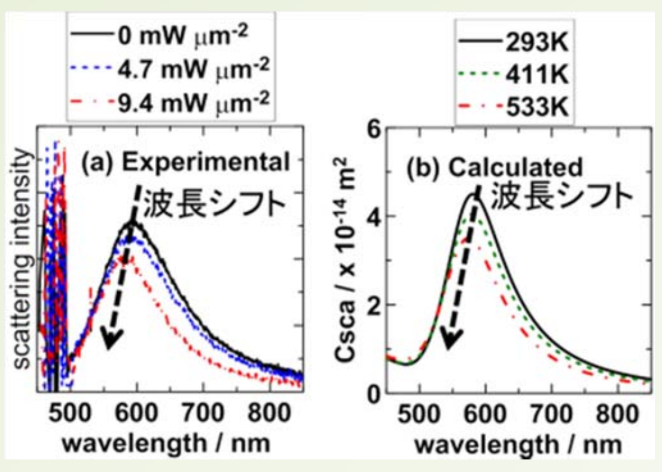
Darkfield image of d = 100nm Au NPs immersed in water and supported on a glass substrate.

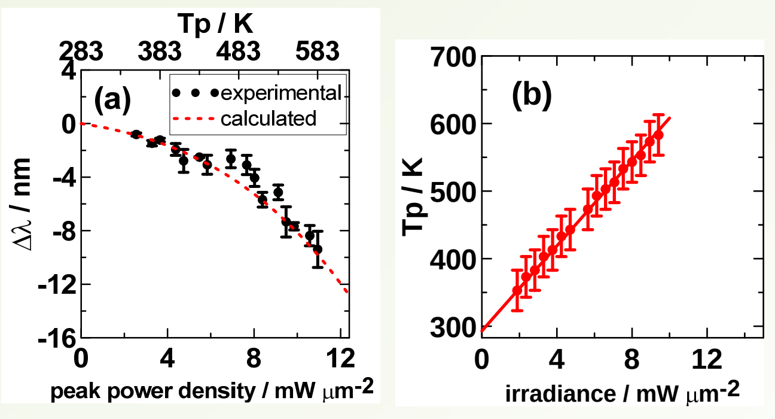






The refractive index of the medium surrounding Au NP is temperature-dependent as for the complex refractive index ε(ω, T) of the Au NP. Therefore, the nonlinear optical properties of Au NP are highly sensitive to the refractive index change in the surrounding medium as a result of temperature increase in the close vicinity of a Au NP.





The blue shifts accompanied by intensity reduction were ascribed to the changes in the conduction electron scattering frequency and the refractive index reduction in water at high temperatures. When the surrounding medium has a greater temperature coefficient of refractive index (such as water, glycerol), appreciable blue shifts occurred due to greater effect of decreased refractive index in the surrounding medium.

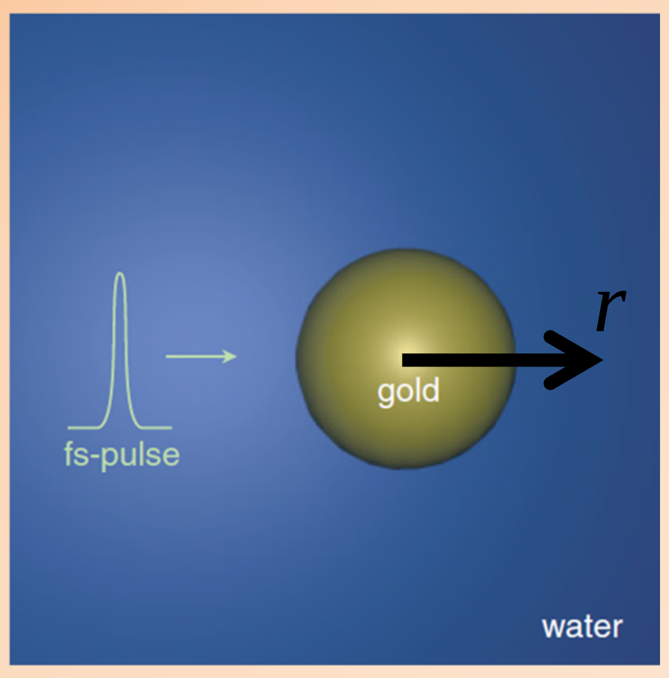
Setoura, *J. Phys. Chem. C*, **116**, 15458, 2012

Theoretical

Baffou, *Phys. Rev. B*, **84**, 035415, 2013

General Heat Diffusion Equation

$$\rho c\, \partial_t T(r,t) = \kappa \nabla^2 T(r,t) + p(r,t)$$



Equations for pulsed-laser heating

$$\begin{cases} \text{Diffusion equations:} \\ \rho_{\mathrm{Au}} c_{\mathrm{Au}}\, \partial_t T(r,t) = \kappa_{\mathrm{Au}} \nabla^2 T(r,t) + p(r,t) \text{ for } r < R, \\ \rho_{\mathrm{W}} c_{\mathrm{W}}\, \partial_t T(r,t) = \kappa_{\mathrm{W}} \nabla^2 T(r,t) \text{ for } r > R. \\ \text{Boundary conditions at } r = R: \\ \kappa_{\mathrm{W}} \partial_r T(R^+,t) = \kappa_{\mathrm{Au}} \partial_r T(R^-,t), \\ T(R^+,t) = T(R^-,t). \end{cases}$$

Equations for steady-state heating

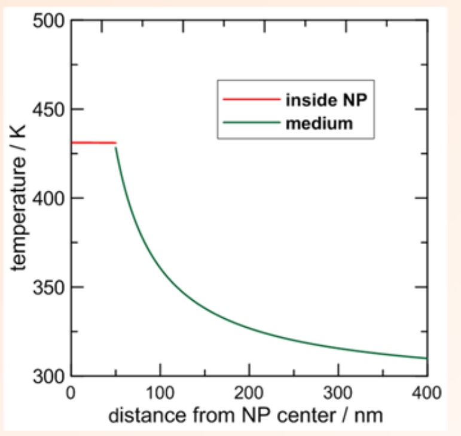
$$T^{\mathrm{cw}}(r) = \frac{\mathcal{P}_0}{4\pi\kappa_{\mathrm{W}} R}\left[1 + \frac{1}{2\gamma}\left(1 - \frac{r^2}{R^2}\right) + \lambda_{\mathrm{K}}\right]$$

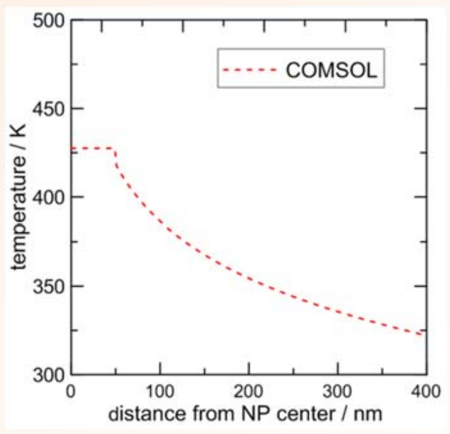
$$T^{\mathrm{cw}}(r) = \frac{\mathcal{P}_0}{4\pi\kappa_{\mathrm{W}} r}$$

thermal conductivity: k [W m^{-1}K^{-1}]
temperature: T [K], NP radius = R [nm]
heat source: $P_0 = C_{abs} \times I$ [W m^{-2}]

Thermal barrier between Au/medium interface

Analytical solutions are available for a CW laser-heated Au NP in homogeneous medium (i.e. steady-state 1-D heat conduction problem). Temperature profiles calculated by analytical solution and computed by COMSOL show quite similar values using same heat source.





d=100nm Au NP in water, I = 1.5 mW μm^{-2}

Note that free convective heat transfer is negligible for nanoscale objects.

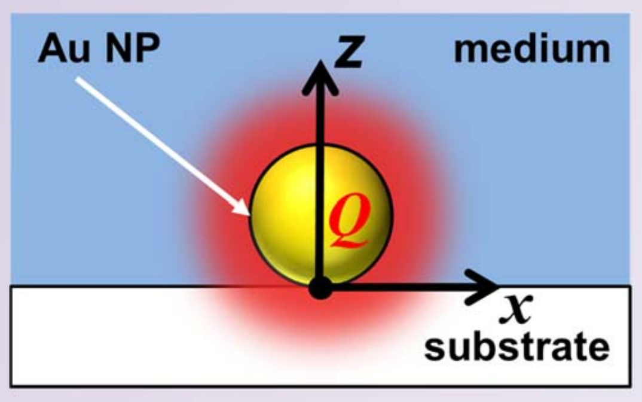
2-D Heat Transfer Analyses using COMSOL

Setoura, *ACS Nano*, **7**, 7874, 2013

Modeling

Heat Conduction Equations

$$\begin{cases} k_{NP} \nabla^2 T(x,z) = Q(x,z) \\ k_{med} \nabla^2 T(x,z) = 0 \\ k_{sub} \nabla^2 T(x,z) = 0 \end{cases}$$



Boundary Conditions $\sqrt{x^2 + (z-a)^2} = a$

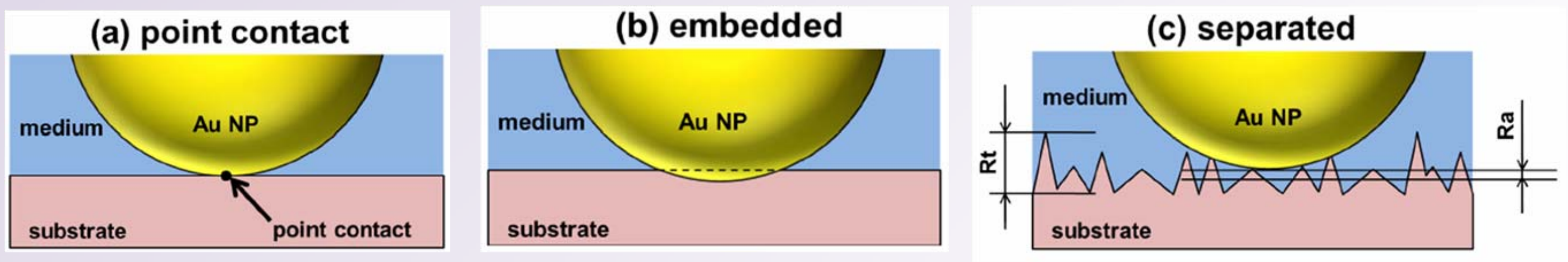
$$k_{NP} \partial_{x,z} T(a^+) = k_{med} \partial_{x,z} T(a^-) \qquad T(a^+) = T(a^-)$$

$$k_{med} \partial_{x,z} T(z^+) = k_{sub} \partial_{x,z} T(z^-) \qquad T(z^+) = T(z^-)$$

thermal conductivity: k [W m^{-1}K^{-1}], temperature: T [K]
NP radius = a [nm], heat source: $Q = C_{abs} \times I$ [W]

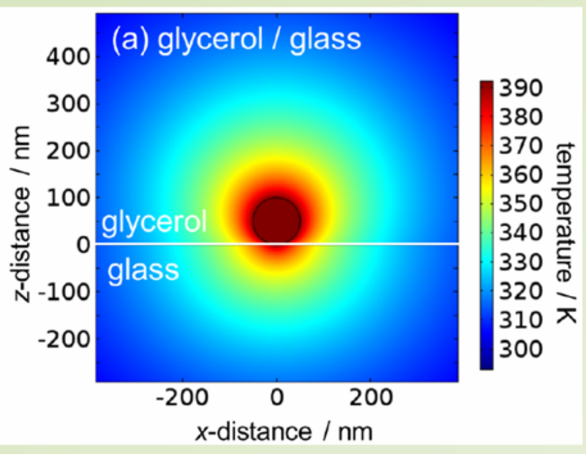
Contact area of Au NP/substrate

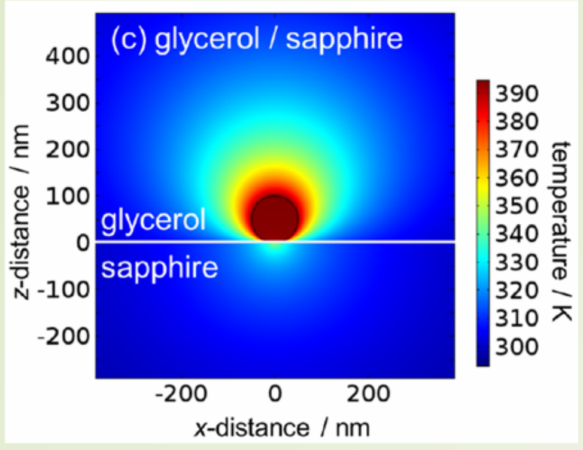
Three contact models are taken into account for computation. (a) Point contact is an ideal contact mode for Au NP and substrate. (b) and (c) considering the average surface roughness of the substrate (±0.3nm) for contact model of NP and substrate.



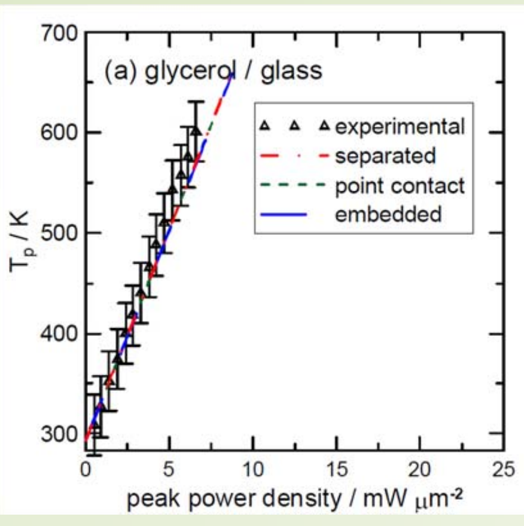
Computational Results

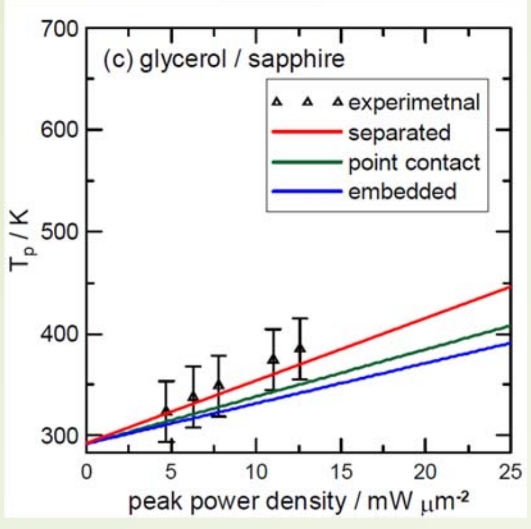
d=100 nm Au NP in glycerol, placed on glass, sapphire.





Computational results by COMSOL reproduce experimental NP temperature increase as a function of peak power density for both glass and sapphire substrates. Because of glycerol's sufficient heat transport ability to the substrates, three contact models show only a slight temperature difference.

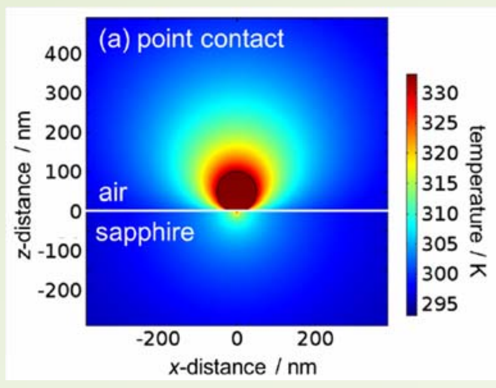


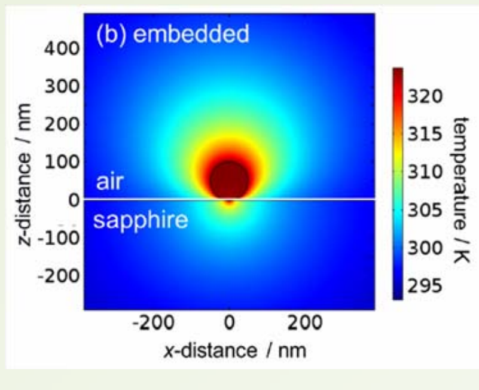


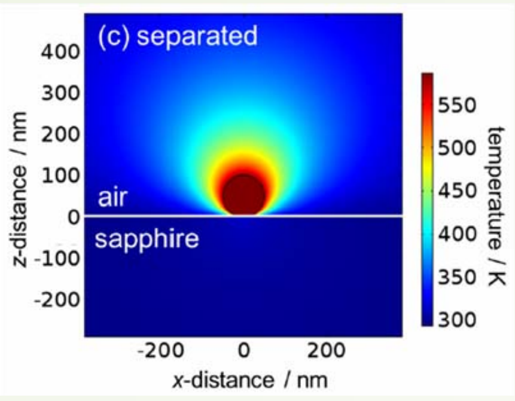
Media and substrates employed for the experiment.

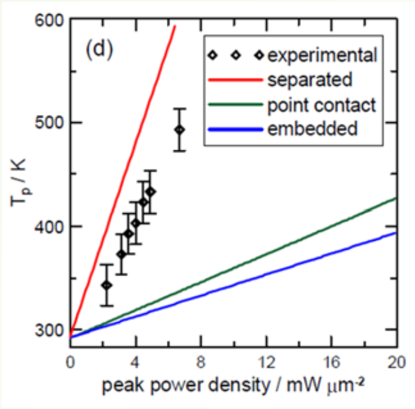
1. air k=0.024 /W m^{-1}K^{-1}
2. glycerol k=0.28 /W m^{-1}K^{-1}
3. water k=0.6 /W m^{-1}K^{-1}
4. glass k=1.0 /W m^{-1}K^{-1}
5. CaF$_2$ k=9.7 /W m^{-1}K^{-1}
6. sapphire k=42.0 /W m^{-1}K^{-1}

d=100nm Au NP in air, placed on sapphire.



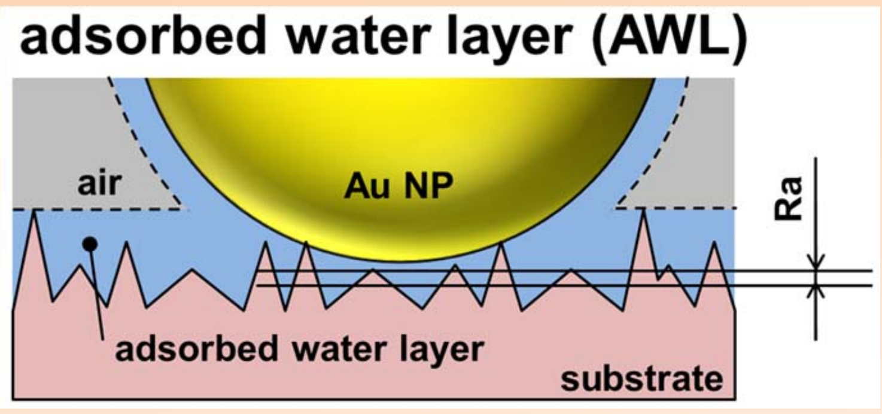






Whereas a temperature increase takes place with smaller slopes for the systems in which the particle and substrate are in contact, a remarkably greater slope was realized by separating the particle from the substrate. This difference arises from air's low thermal conductivity that makes to act as a thermal insulator, preventing heat conduction to the substrate. The separated model gave a better agreement with the experimental laser intensity-particle temperature relationship

Effect of adsorbed water layer



An adsorbed water layer (AWL) with thickness of a few nanometers comes from the substrate surface in an ambient atmosphere. Practically, AWL may play a major role of transporting thermal energy from NP to substrate at relatively low temperature. Therefore, we have considered AWL to a separated model. AWL thickness was set to 1.0nm.