Optical manipulation and study of single gold nanoparticles in solution

Ruijgrok, P.V.

Author: Ruijgrok, Paul Victor
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Conclusions and perspectives

In this thesis we have investigated the optical trapping of single gold nanoparticles, as a novel approach to study single metal nanoparticles in solution, and to explore the use of a single metal nanoparticle as an ultra-small tool to enable mechanical manipulations on the nanometer scale. Here we conclude by summarizing the main arguments, reviewing the main results and providing a perspective on future work that may be enabled by the methods presented in this thesis.

7.1 Thesis conclusion

7.1.1 Study of single nanoparticles in solution

We have argued that the study of single gold nanoparticles in solution has potential as an approach to resolve nanoscale phenomena. The benefit of single-particle studies originates from the observation that no two nanoparticles are ever exactly alike; a given sample always presents a distribution of particle sizes and shapes. As the properties of the particles, and the processes taking place on those particles, are functions of the particle size and shape, a distribution of particle properties results. Single-particle studies give access to the full distribution of particle properties, and the correlation of multiple properties on the same particle. Time-dependent phenomena can be studied without the need for ensemble-wide synchronization, and study of stochastic processes becomes possible. The interest in the study of particles in solution results from the observation that a variety of physical processes intrinsically takes places in solution, and that immobilization on a solid surface –the commonly taken approach to study single nanoparticles– may introduce unwanted perturbations. A study of particles in a homogeneous liquid environment prevents unknown, local nanometer-scale interactions with a solid surface, facilitating direct comparison with theoretical models.

In this thesis we have used an optical trap as a means to confine a single nanoparticle in solution to the focal spot of a microscope objective. We have demonstrated that with this approach a single nanoparticle in solution could be studied with a variety of optical techniques for practically unlimited times. Observation times up to several hours were demonstrated, but this was limited by the patience of the author rather than by any principle limitation.

As a first demonstration of an experiment that benefits from this geometry, we have studied the mechanical vibrations of gold nanoparticles with time-resolved optical techniques. For the first time we could directly measure the homogeneous damping time of the acoustic vibration of a single gold nanoparticle in a homogeneous liquid environment. Surprisingly, these damping times were a factor of 2-3 shorter than predicted by the commonly used theory – well tested in macroscopic systems– that considers acoustic energy loss by radiation of sound waves into the environment. Also, the observed vibrational damping time varied largely for individual particles, by more than a factor of two. We concluded that damping mechanisms other than radiation losses contribute significantly to the damping of the vibrations of nanoparticles. Although part of the dissipation may originate from the organic capping layer surrounding the particles, the current hypothesis is that a significant fraction of the total damping of the vibration is contributed by internal friction in the metal nanoparticle itself. Particle-to-particle variations in crystal structure and the number of crystal defects may cause the particle-to-particle variation in damping times.

7.1.2 Optically trapped single gold nanoparticles as a mechanical tool

We have argued that optically trapped single gold nanoparticles have potential to be used as tools to perform local nanoscale mechanical manipulations in solution and in complex soft-matter environments that are inaccessible to other mechanical tools.

Due to their conduction electrons, metals have higher polarizabilities than dielectric materials. In a metal nanoparticle, this polarizability is enhanced further due to the surface plasmon resonance. Even more importantly, the effect of the plasmon resonance is to concentrate the absorption profile in a narrow region around the resonance, so that the absorption at infrared wavelengths becomes small –in stark contrast to bulk metals– and appreciable optical forces can be exerted without excessive heating and the resulting detrimental radiation pressure. In practice, polarizabilities of nanoparticles at infrared wavelengths can be 20-50 times larger than those of typically used dielectric materials as glass or polystyrene. Gold nanoparticles can be trapped down to 10 nm in size, whereas trapping of dielectric particles smaller then several hundred nanometers becomes difficult. The reduced size of the nanoparticles may be beneficial for applications where the allowable space for a probe/actuator is limited, or for heterogeneous systems were the probe size limits the spatial resolution.

In this thesis we have explored the potential of single metal nanoparticles as mechanical actuators by demonstrating the novel optical trapping features that are enabled by the optical properties of single gold nanorods. Firstly, the gold nanorod can be trapped with larger forces –or down to smaller sizes – due to the high polarizability associated with the narrow longitudinal surface plasmon resonance. Secondly, the polarizability of the rods is also highly anisotropic, dominated by the dipolar dependence of the longitudinal plasmon resonance. This leads to an optical torque that aligns the rod along the polarization of the trap. We demonstrated that an optical torque of up to 100 pN·nm could be exerted on a nanorod of 25 nm diameter and 60 nm length, with a trapping power of 80 mW. This torque would be large enough to allow mechanical manipulation of relevant single (bio-)molecules such as DNA. Simultaneously, optical forces up to a few tenths of pN can be exerted on the trapped rod. The simultaneous application of these relatively large forces and torques on an ultra-small particle could enable optical manipulation in living cells.

The measurements of the optical forces and torques on the single gold nanorod were obtained from a study of the Brownian motion of the particle in the trap. Several novel methods were developed in this thesis to allow the simultaneous observation of the translational and rotational Brownian motion of the trapped rods, making use of the rod's anisotropic light scattering properties. By measuring the orientational and translational trap stiffnesses as functions of trap power, we could determine the temperature of the particle in the trap. We found heating rates around 0.5-1 K/mW, resulting in particle temperature increases around 40-80 K at the used trap powers. For biological applications these temperature increases are of concern. However, we anticipate that heating rates may be further reduced, and methods can be developed to circumvent detrimental effects resulting from this heating (see Perspectives).

The study of the temperature-dependent dynamics of the translational and rotational Brownian motion also resulted in a surprising finding about the Brownian motion of a hot particle. Firstly, our results experimentally confirmed a recently developed theory for the translational diffusion of a hot particle, moving in an inhomogeneous viscosity and temperature profile. The translational fluctuations can be described by an effective temperature, close to the average of the particle temperature and the temperature of the environment. Secondly, we found that the rotational Brownian motion must be described by a higher effective temperature. Although we suggested several possible explanations in Chapter 4, this effect was not fully understood. After publication of our work, theoretical physicists from Leipzig immediately started to think about this surprising result. Very recently an analytical theory has been developed,[92,198] showing that our results are quite generally valid for Brownian motion of hot particles, both for spheres and rods. The reason that the rotational Brownian motion must be described by a different temperature than the translational Brownian motion is that the velocity profile around the particle moving through a liquid is different for the two types of motion. The velocity profile for rotational motion follows a steeper spatial decay (scaling as $1/R^3$) than the profile for translational motion (scaling as $1/R$). As a result, the rotational motion is most sensitive to properties close to the particle, where temperatures are highest and viscosities are lower.

7.1.3 Overview of results obtained in this thesis

Here we list as concise statements what we believe to be the most important scientific findings obtained in this thesis, with reference to the Chapters in which they were reported.

1. The signal-to-noise ratio in photothermal detection of absorbing nano-objects can be enhanced by i) choice of a liquid surrounding the particle with optimal photothermal properties (high $\partial n/\partial T$, high n and low heat capacity/thermal conductivity); ii) using a detection laser with a wavelength outside of the absorption band of the absorber and the highest possible intensity; iii) by thermal isolation of the absorber from the glass substrate.
   Chapter 2

2. A trapped single gold nanorod of 25 nm diameter and 60 nm length can serve as a simultaneous transducer of forces ($\sim 0.1 - 1$pN) and torques ($\sim 10 - 100$ pN·nm), large enough to enable mechanical manipulation of relevant single (bio-)molecules.
   Chapter 4

3. The translational and rotational Brownian motions of a hot nanoparticle are described by different effective temperatures. The temperature of rotational Brownian motion is closest to the particle temperature.
   Chapter 4

4. The damping of acoustic vibrations of gold nanoparticles is determined both by radiation of sound waves to the environment and by intrinsic dissipation in the nanoparticle.
   Chapter 6

7.2 Perspectives

The results in this thesis demonstrate the potential of studying single particles in solution with the aid of an optical trap, and the promise of optical trapping for the use of gold nanoparticles as mechanical tools. Here we discuss directions that could be taken, in the immediate and near future.

7.2.1 Deposition of trapped particles on a solid substrate

For a variety of experiments it would be valuable to study a single nanoparticle in the optical trap in solution, subsequently deposit the particle on a solid substrate and repeat the performed measurements. Such experiments would enable the direct probing of the optical, thermal and mechanical effects of the substrate. Additionally, once the particle is immobilized, the coverslip can be taken to an electron microscope to determine the exact morphology of the particle that was studied.[166,170] The deposition of optically trapped particles on substrates has been demonstrated by several authors.[199,200] Aided by the specially designed flow-cell (Appendix B), this type of experiments can be performed immediately.

7.2.2 Focal engineering

The quality of optical trapping is determined by the gradient of the light intensity that can be created. As in so many applications in microscopy, this ultimately boils down to the requirement to create the smallest possible focal spot. This requirement is especially challenging in optical trapping applications; the near-infrared wavelengths that are typically used fall outside of the wavelength range for which commercially available microscope objectives are optimized, and frequently spherical aberrations are introduced when trapping is performed many microns away from a glass surface. In this thesis we have already seen the importance of these spherical aberrations for optical trapping, and the need to compensate them with inventive methods.

In recent years there have been much developments in the engineering of beam foci by altering the phase and amplitude profiles of an incoming beam with spatial light modulators.[201,202] With these methods, optical trapping of dielectric particles through a turbid layer has been demonstrated.[203] We anticipate that these methods can help to overcome the limitations of commercial microscope objectives at near infrared wavelengths and improve the optical trapping of metal nanoparticles.

A different approach comes from the realization that the properties of a focus depend on the polarization structure of the beam.[204] Besides the familiar linearly or circularly polarized Gaussian beams, Maxwell's equations allow solutions with many other polarization structures, that can have surprising properties. In particular, the focus of a radially polarized beam can be both tighter than the focus of the linearly polarized beam,[116] and be almost completely longitudinally polarized.[205] A property accompanying the latter effect is that the longitudinal component of the Poynting vector vanishes at the focus.[206] For optical trapping of metal nanoparticles, this has the important consequence of eliminating radiation pressure, that normally results from absorption of the trap laser. This leads to a deeper potential for a given trap power or, conversely, a reduced heating of the trapped particle for a given trap depth. For typical conditions as reported in this thesis, the temperature increase of the particle may be reduced by about a factor of two for the same achieved trap depth.

7.2.3 Single-particle studies in solution

With practically unlimited observation times on single metal nanoparticles in solution, a variety of exciting applications comes within reach. Here we think of problems in nanoscale heat conduction,[207–210] and the formation of a vapor-shell around a hot nanoparticle.[211,212] The formation of a vapor-shell around a nanoparticle is an interesting thermodynamic problem in itself, but may also enable practical applications. For example, these nanobubbles have already been used to enhance the effectiveness of cancer therapies.[213] Reports thus far have focused on the case where bubbles are formed transiently, by heating of the metal nanoparticles with short optical pulses. If conditions for stable vapor-shell formation can be found, the trapped gold nanoparticle can be effectively studied in gas-phase. Another exciting direction is the study of nanoparticle catalysis. Since the pioneering work of Haruta[214] in 1989 it is known that gold nanoparticles can be efficient catalysts.[215] Catalysis is performed both in the gas-phase with supported nanoparticles and with nanoparticles in solution.[216] Study on single particles in solution may provide new insights into the heterogeneous nature of catalysis.

7.2.4 Manipulation of bio-molecules

One of the methods that has revolutionized biophysics in the last decades has been the application of optically trapped particles to mechanically manipulate single bio-molecules *in-vitro*. Thus far, these studies have been performed exclusively using dielectric particles. Concern about laser-induced heating of metal nanoparticles has most likely been the reason that metal nanoparticles have not been used for single-molecule manipulation.

We advocate here that such trials should be made nevertheless, to characterize to what degree the attached bio-molecules are affected. Additionally, we suggest that continued efforts should be made to i) reduce the laser-induced heating and ii) find inventive ways to circumvent any detrimental effects of heating on the biological system of interest. Specific possibilities of the first include the optimization of optical trapping by focal engineering as addressed above. As a possible method to contribute to the latter we suggest to make use of the steep decay ($1/R$) of the temperature around the particle, for example by using particles with a silica coating. Such a coating does not affect significantly the heating of the particle or the resulting temperature, but simply serves as a heat resistant layer that keeps the bio-molecules at a safe distance.

7.2.5 Trapping in living cells

In this thesis we have advocated the use of optically trapped metal nanoparticles in crowded environments. The prime example of such an environment is a living cell. Our vision, perhaps rather naive, is to study the mechanical properties of cellular components and/or single molecules in their natural environment. Of course, the challenges are great. However, we advocate that such experiments simply be tried, and their limits explored. One of the challenges to overcome is the effect of trapping beam aberrations that result from the refractive index variations in the cell. We believe that significant progress can be made here using adaptive optics. An additional complication is that cellular components may move, so that the trapping beam will have to be adapted dynamically. Whether, or to what degree, the laser-induced heating of the metal nanoparticles will affect cellular experiments remains to be characterized. Even if heating turns out to be too great an obstacle to enable non-destructive single molecule manipulations in the cell, we anticipate that trapped metal nanoparticles can be used otherwise, for example to perform some form of nanoscale surgery.