SOCIETY OF PHYSICS STUDENTS

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# SPS Chapter Research Award Proposal

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| Project Proposal Title | Deducing size and shape of Gold Nanorods in solution from Depolarized Dynamic Light Scattering data |
| Name of School | Cleveland State University |
| SPS Chapter Number | 1247 |
| Total Amount Requested | $1,990 |


## Abstract

To further our understanding of light scattering by a solution of anisotropic, hard-to-image, soft particles, such polypeptide micelles or polymeric microgels, a coupled approach of depolarized dynamic light scattering characterization and SEM imaging of anisotropic, easy-to-image, and inorganic gold nanoparticles will be undertaken. Commercial gold nanoparticles: nanospheres and nanorods of various aspect ratios will be used.

# Proposal Statement

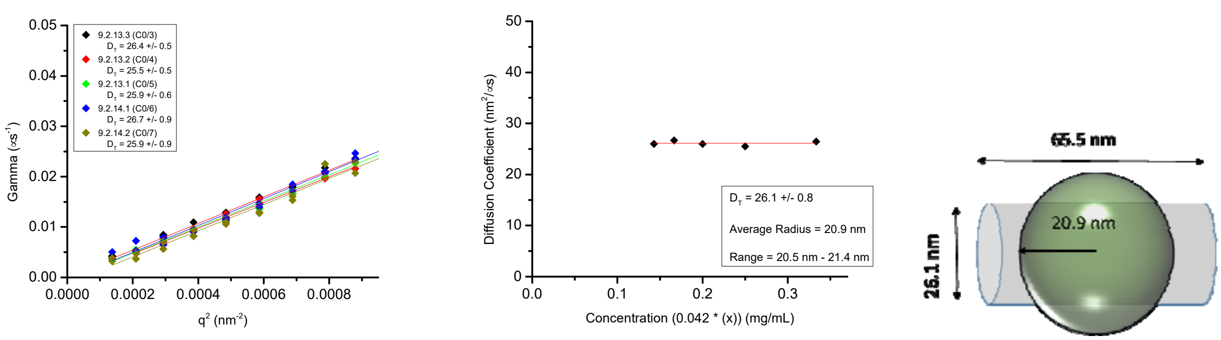
The entire Proposal Statement should be no more than 4 pages, and organized as follows.

## Overview of Proposed Project

Studying structure, dynamics, and composition of anisotropic water-based environmentally-sensitive nanoparticles (such as protein and polymeric micelles) in solutions presents a serious challenge. These soft matter systems are notoriously challenging to image with electron or other types of microscopy as they are easily affected by an electron beam and change their configuration with change of environmental variables such as temperature and pH. To this end the Depolarized Dynamic Light Scattering (DDLS) is a powerful in situ method that allows studying the micelles without damaging them. However, interpretation of the DDLS results on anisotropic particles in solution still presents a serious challenge. To this end we propose to study gold nanorods of different aspect ratios by two parallel methods: DDLS and SEM. The parallel use of the two methods should allow us to test assumptions of the elongated particle diffusion models and determine the limitations of DDLS technique. Understanding these limitations will become very useful in suing DDLS for studies of soft matter systems that are hard to image. Three active members of our chapter have already worked on different parts of this project before and all three plan to complete an Independent study on it.

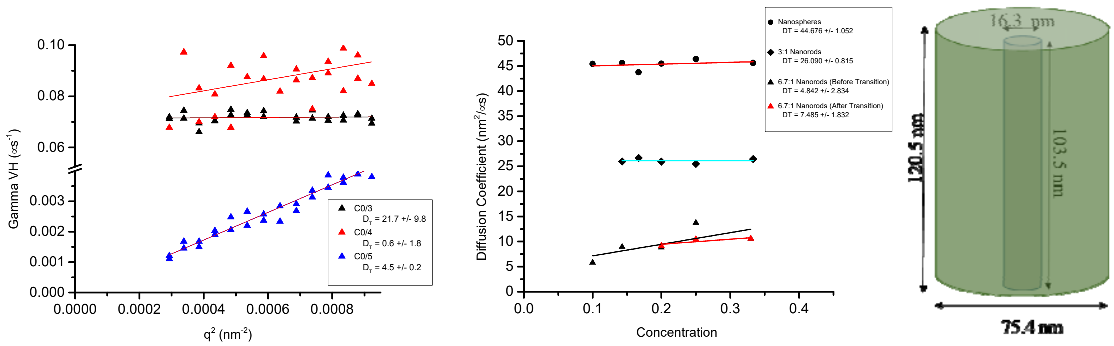
## Background for Proposed Project

DDLS indirectly measures the rotational and translational diffusion of nanoparticles suspended in solution using the properties of the correlation functions. The particle size, shape, and intermolecular interactions can then be deduced from the DDLS data by using models of diffusion for particles of various geometry. While the scattering by spherical nanoparticles is well understood, the scattering by anisotropic particles is difficult to interpret. Our preliminary studies of gold cylinders (1) show that extra care should be taken in trying to understand the light scattering data on any sample of elongated particles. For example nanorods of small aspect ratio might not yield apparent signature of anisotropy in a DDLS experiment. Indeed, as was shown in Ref1, nanorods with 3x1 aspect ratio behaved in the same way isotropic particles would (Figs 1A, 1B below). Indeed, no observable VH signal was detected and the angular dependence of light scattering was consistent with spheres of R=20.9nm. SEM on the same nanorods revealed particles of size 26.1 x 65.5 nm (Fig 1C, compares results of DDSL and SEM).




This interesting result points to certain limitations of the DDLS technique in current version for studying small aspect ratio elongated particles. The consequences of the result also should be considered seriously as it is apparent that the light scattering (DLS or DDLS) by elongated particles with small aspect ratio can be misinterpreted and mistakenly attributed to spherical geometry of particles. This interpretation would be more likely for soft-matter systems that are hard to directly image.

On the other hand, gold nanorods with stronger anisotropy (6.7:1) revealed the properties characteristic of elongated particles (1). In particular, a strong VH signal was observed (shown as a decay rate of correlation functions on Fig 2A, below) and a noticeable concentration dependence of the VV decay rate (Fig. 2B, below)) that was absent from the samples of spheres and smaller aspect ratio (3:1) cylinders. Unfortunately, the experiments on 6.7:1 cylinders were incomplete as the samples aged significantly. As a result, the obtained data was too noisy to get a reliable estimate of the cylinder dimensions (the estimates appear on Fig 2c). Finishing, this set of experiments and obtaining the more reliable estimate for the size of 6.7:1 aspect ratio cylinder would be the first goal of this proposal.




After completing characterization of 6.7:1 aspect ratio cylinders we would like to look at the cylinders of higher aspect ratios (8:1, 10:1, 17:1) to see the limitations of our DDLS experimental method. The overall emphasis in this project would be to formulate a robust experimental DDLS method and mathematical model that reproduces the measured rotational and translational diffusion of elongated particles of various aspect ratios. In order to account for distinct non-spherical geometries, the respective correction factor is incorporated into the Stokes-Einstein equation. Additional correction might be needed to take into account the effect of the concentration of particles and their potential interaction. The size dimensions from the DDLS experiment will be compared to the size distribution from SEM images (since gold nanorods do not change their geometry upon drying it is easy to image them with SEM)

The establishment of such a model for interpreting the light scattering data of easily imaged samples (such as gold nanoparticles or FeOOH spindles (2,3)) can be utilized on more complex wet systems, such as micelles, microgels, and protein complexes that cannot be easily imaged via electron microscopy, which has the potential to expose the sample to a detrimental environment.

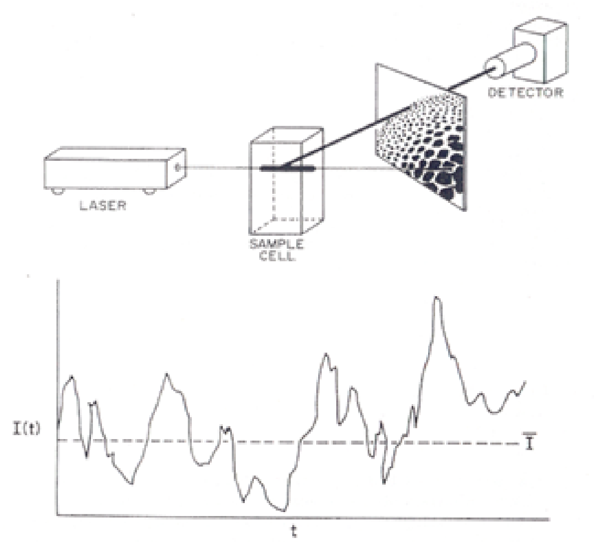
In order to succeed in creation of such a model a set of commercially available, reproducible, and easily imaged samples should be studied. We propose to do a study of gold nanoparticles both of spherical and cylindrical geometry. Using spherical and cylindrical particles of the same composition and diameter would promote success in relating scattering from well understood spherical particles and from less understood cylindrical particles. The aspect ratio of the elongated particles will be significantly varied to allow better understanding of the role of the length on rotational diffusion.

## Expected Results

The project aims to develop an experimental method that reliably deduces the dimensions of cylindrically -shaped gold nanorods using the rotational and translational diffusion data obtained from DDLS. Currently, deducing sizes for the prolate ellipsoid has been successfully accomplished on the example of FeOOH spindles(2,3). The primary objective in continuing this research is to obtain a comprehensive method that can characterize the size and anisotropy of nanoparticles of soft matter in solution systems that do not have the capability of being directly imaged using other various techniques, i.e. electron microscopy. The limitations of the method need to be addressed. In addition, the effect of the plasmon resonance in the gold nanoparticles, seen in preliminary studies, on the diffusion of particles will be studied, in order to confirm the validity of our method.

## Description of Proposed Research - Methods, Design, and Procedures

Quasielastic light scattering, also referred to as dynamic light scattering (DLS), is one of the most noninvasive methods of obtaining particle diffusion within a solution. DLS begins with the measurement of light intensity fluctuations caused by incident laser light scattering off the surface of particles in solution. When applied to dilute, monodisperse solutions in thermal equilibrium, the translational diffusion coefficient ($D_{VV}$) obtained by DLS can be used to estimate the size of particles in solution from the Stokes-Einstein equation. However, there are some assumptions to be made when utilizing the Stokes-Einstein equation. First, it must be assumed that the solution in question is infinitely dilute. Second, it is assumed that the particles within solution are monodisperse. Finally, the solution must exclusively contain spherical particles. With these three assumptions, the hydrodynamic radius ($R_H$) can be calculated via $D_{VV}$ obtained from the Stokes-Einstein equation (Fig D, Ref 2).




$$D = \frac{kT}{6\pi\eta R}$$

Stokes-Einstein

$$R_H = \frac{kT}{6\pi D \eta_o}$$

Hydrodynamic Radius

(Note: a proper $D_{vv}$ measurement requires DLS experiments to be done at multiple angles in order to check the angular dependence of the decay rate (G). When studying solutions of anisotropic nature, however, basic DLS fails, as it assumes spherical particles in the analysis. The introduction of a depolarizer into the DLS system allows for DDLS. Unlike spherical particles whose motion is described only by a translational diffusion coefficient ($D_{VV}$), geometrically anisotropic particles yield a measurable rotational diffusion coefficient ($q_{VH}$). The depolarizer allows the analysis of scattered light both in vertical and horizontal polarization, which in turn provides not one, but two unique correlation functions which are characterized by a translational decay rate ($G_{VV}$) and a rotational decay rate ($G_{VH}$). These two quantities can then be used to obtain the particles' translational and rotational diffusion coefficients and apparent length and width.

## Plan for Carrying Out Proposed Project

- The three students will be cooperatively working on this project: Ilona Tsuper, Dan Terrano, Tony Dobrila. They are all active SPS members.
- Two of the students (Dan and Ilona) will work together on gathering additional DDLS data on small-medium aspect ratio nanorods (4.5:1, 6.7:1, 8:1), analyze the results, and research various literature to obtain the needed correction factors in the Stokes-Einstein equation for the cylindrically shaped nanoparticles and corresponding diffusion models. Both students plan to work on two-semester long independent study on diffusion of elongated if the proposal is funded. (Spring 17, Summer17)
- The third student (Tony Dobrila) will collect DDSL data for diffusion of large aspect ratio nanorods (10:1, 17:1), analyze it, will help in the development of the modeling, in particular, by studying the effect (or lack of thereof) of plasmonic resonance on gold nanoparticles. He is planning to take his independent study in the Summer-Fall17.
- The research will be conducted at Cleveland State University in the Department of Physics.

- Dr. Streletzky will oversee the project and will allow the students to use his lab and utilize the laser.

## Project Timeline

Our inventory currently contains aging gold nanorods of small aspect ratios, the next step in the process is in purchasing and obtaining gold nanorods with intermediate and large aspect ratios as well as fresh samples of small aspect ratio nanorods. Funded proposal will allow us to continue conducting DDLS experiments to further explore nanoparticles of small-to-large aspect ratios. In the spring of 2017, two of the students will conduct preliminary analysis on the small-medium aspect ratios for the nanoparticles that are being used in developing the current model. Concurrently, literature research will be taking place to understand the relevant correction factors needed for the Stokes-Einstein equation. All findings will be documented and presented in the submission of the interim report (May 31, 2017). In the summer of 2017, another student will join the group by helping with DDLS experiments on larger aspect ratio nanorods and by exploring the occurrence of Plasmon Resonance for the newly obtained nanoparticles with the continuation of DDLS experiments and analysis. All findings will not only be documented and presented in the final report (December 31, 2017), but will also be presented at the annual APS March Meeting of 2018.

## Budget Justification

Purchasing stable, reproducible, and easily imaged by SEM samples of gold spheres and nanorods of the same diameter and composition will allow direct comparison of light scattering results from two different geometries. This should lead to a more robust model for interpreting light scattering by cylindrical particles. Using cylinders of different aspect ratio will allow testing the validity of this model for the cylinders of different length.

Dr. Streletzky's light scattering lab DDLS set up and lab supplies will used for the experiments. Ilona Tsuper and Dan Terrano will use this project as the topic for their Independent Study work in the Spring –Summer 17, while Tony Dobrila will continue the work on this project in the Summer –Fall 17 for his own Independent Study.

## Bibliography


1. *"Optimizing Dynamic Light Scattering for the Analysis of Anisotropic Nanoparticles in Solution"* Tony D. Dobrila, Kiril A. Streletzky, **10th Annual CSU Undergraduate Research Symposium**, Sep 1, **2016;** Fall16 OSAPS meeting (Bowling Green SU)**,** Oct **7, 2016.**
2. *"Deducing Shape of Anisotropic Particles in Solution from Light Scattering: Spindles and Nanorods"*, I. Tsuper, D. Terrano, K.A. Streletzky, O. Dement'eva, S. Semyonov, V. M. Rudoi, ***Bull. Am. Phys. Soc. 61(1)*** G1.00104 **(2016) APS March Meeting**, (Baltimore, MD, Mar 15); **Fall15 OSAPS/Zone 7 Meeting,** CSU, Oct17**, 2015;** ***COSHP Research Day***, April 8, 2016.
3. K. A. Streletzky, P. Dee, O. Dementeva, V. Rudoy, "Characterization of FeOOH spindles in solutions with in situ DDLS", submitted to *Colloidal Journal*