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Project title:
Long Range van der Waals - London Dispersion Interactions
For Biomolecular and Inorganic Nanoscale Assembly

Names of the PIs: Roger H. French, Nicole F. Steinmetz

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Final Report

I. Executive Summary:

This was a collaborative project including the research of UMass (PI Adrian Parsegian) and his collaborators at University of Missouri-Kansas City (Ching). Long range interactions (LRIs) play a critical role in the formation of mesoscale self-assemblies. A thorough understanding of LRIs (including van der Waals, electrostatic and polar interactions) in inorganic and organic systems facilitates the design and construction of novel heterogeneous assemblies. Through this project, we have enhanced the understanding of LRIs in a few aspects: 1. We investigated the electronic structures and full spectral optical properties of inorganic systems AlPO4 and SiC, and analyzed the van der Waals interactions of these systems; 2. Fully retarded solutions to the Lifshitz formulations (which is used to calculate Hamaker coefficients of van der Waals interaction) for a range of new system geometries have been implemented into open-source program Gecko Hamaker, making it possible to evaluate the van der Waals interaction of complex optically and morphologically anisotropic objects such as collagen, DNA and single-walled carbon nanotubes; 3. The electronic structure and LRIs in typical biomolecular systems under various biophysical conditions were investigated comprehensively; 4. The structure-optical property relationship of some biomolecules (such as DNA oligonucleotides) were revealed. We have also demonstrated a LRI-driven energy harvesting self-assembly via experimental measurements and numerical modeling. This project lay the foundation for future development of heterogeneous self-assembly.

II. Comparison of the actual accomplishments with the goals and objectives of the project

In this collaborative project, we proposed to investigate the spectral optical properties and long range interactions (LRIs) of inorganic and biomolecular systems, so as to guide the design of functional mesoscale assemblies driven by LRIs, including the van der Waals (vdW),

electrostatic ES) and polar (P) interactions. We targeted specific inorganic and biopolymers, such as silica, aluminum phosphate, DNA and collagen.

We have focused on the objectives and goals by directing our research activities in a few areas: measure and calculate the electronics structures and spectral optical properties of the focus materials, and derive the full spectral van der Waals (vdW) interactions; characterize intermolecular interactions directly using light scattering methods; implement new numerical solutions for vdW interaction potential into open source program Gecko Hamaker. We then demonstrated LRI driven mesoscale assembly by building the first biopolymer-based LRI-driven self-assembly for energy harvesting application. We have achieved the accomplishments of the proposed project.

III. Summarize project activities for the entire period of funding

1. Original hypotheses

Long range interactions, present at distances longer than an interatomic bond length, play an essential role in mesoscale assembly of heterogeneous systems. Of the LRIs (consisting of vdW, ES and Polar interactions as their fundamental component interactions), the vdW interaction is universal and serves to set the magnitude of the interparticle interactions that can be manipulated. Therefore from a detailed knowledge of how to control and vary the vdW interactions, new control of mesoscale assemblies can arise.

2. Approaches used

A combination of VUV spectroscopy and spectroscopic ellipsometry were used to measure the full spectral optical properties of $AlPO_4$ and 6H-SiC crystals. Orthogonalized linear combination of atomic orbitals (OLCAO) variant of the density functional theory (DFT) method was used to calculate the electronic structure and full spectral optical properties of the inorganic crystals and DNA oligonucleotides, and providing insights into the electronic origins of the optical features. Liftshiz theory was employed to calculate the retarded Hamaker coefficients of the vdW interactions based on the full spectral optical properties. New optical spectra and LRI solutions was implemented into the open source program Gecko Hamaker. UV-Vis spectrophotometry was performed on DNA solutions to determine the decadic molar absorption coefficient of DNA oligonucleotides. The pairwise self-interaction of biomolecules (bovine serum albumin, native & PEGylated cowpea mosaic virus (CPMV), duplex & quadruplex DNA oligonucleotides) were characterized with composition-gradient multi-angle light scattering method. Computational optics modeling was used to simulate the interaction between light and supramolecular assemblies, and to optimize the structural design of the assemblies.

3. Problems encountered and departure form planned methodology, and an assessment of their impact on the project results

No problems were encountered that required a departure from our research plan.

4. Facts, figures, analyses used during the life of the project to support the conclusions.

1. Measure and calculate electronics structures and spectral optical properties, and derive retarded Hamaker coefficients of the van der Waals (vdW) interactions

1a) Optical Properties and van der Waals Interactions in Berlinite Aluminum Phosphate and silica (CWRU, UMKC)

The complex optical properties of single-crystal berlinite $AlPO_4$ were studied between 0.8 and 45 eV via VUV spectroscopy and spectroscopic ellipsometry. The interband transition features were indexed with respect to the underlying electronic structure. Strong similarities were observed between $AlPO_4$ and its structural isomorph SiO_2 in the excitonic and interband transitions. Hamaker coefficients for $AlPO_4$-based systems with various interlayers were evaluated using the Lifshitz method of the Gecko Hamaker program. The electronic structure and interband optical properties are comparable to those of both quartz and amorphous SiO_2, suggesting that the PO_4 tetrahedra--similar in structure to SiO_2 tetrahedra--are responsible for the electronic structure and interband optical properties. The dominance of PO_4 on the interband optical properties and vdW-Ld behavior of $AlPO_4$ indicate that the phosphate complex ion may play a central role in the electronic structure and intermolecular interactions of phosphate-containing materials ubiquitous in biological systems, including apatites, DNA, and phospholipids.

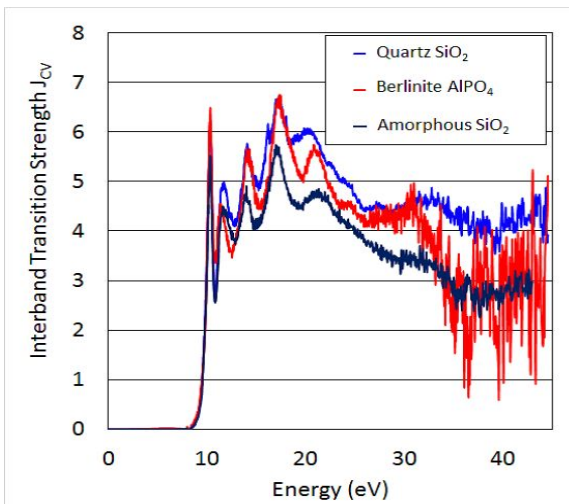

Fig.1 Re(J_{cv}) for berlinite $AlPO_4$, quartz SiO_2, and amorphous SiO_2

1b) Optical Properties and van der Waals Interactions of 6H-SiC (one journal paper in preparation) (CWRU)

Crystalline SiC is an important material in contemporary photoluminescence, detection & storage devices, as well as MEMS/NEMS systems. Understanding the LRIs of SiC is critical for optimizing the fabrication methods of SiC components. 6H-SiC crystal sample was measured with VUV spectroscopy and spectroscopic ellipsometry. Full spectra complex optical properties were determined, and interband transition features were correlated with the underlying electronic structure investigated in an article published by Wai-Yim Ching's group. Hamaker coefficients of 6H-SiC systems were calculated.

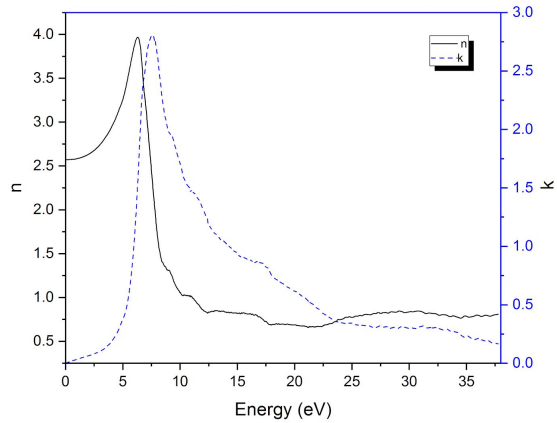

Fig. 2 Complex optical properties of 6H-SiC determined from a combination of VUV spectroscopy and ellipsometry.

1c) Role of Single Interatomic Bond Transitions in Long Range Interactions and Excitons in SiO_2 (UMass, CWRU, UMKC)

The presence of narrow excitonic peaks in the optical spectra of SWCNTs motivated the study of their effect on the Hamaker coefficient for vdW-Ld interactions. UMass formulated a theoretical approach that shows how a change in the dielectric response over a narrow frequency interval has complicated consequences on the vdW-Ld interactions. Optical properties of amorphous SiO_2 (a-SiO_2) glass were calculated (UMKC) and compared with experimentally determined spectra (CWRU), which contain an excitonic peak. The effect of the excitonic peak on the vdW-Ld interactions was then studied. The results show that the effect depends crucially on the position and intensity of the peak, and that the peak position affects all the terms in the Matsubara frequency summation in a non-monotonic fashion. Contrary to the common wisdom, the presence of an additional optical peak does have an affect on the magnitude of the the Hamaker Coefficient across all Matsubara frequencies, not just those at energies near the optical peak.

1d) Structure-optical property relationship of duplex and G-quadruplex DNA oligonucleotides (two journal articles in preparation) (CWRU, UMKC)

A combination of UV-Vis optical absorption experiments and ab-initio quantum mechanical calculation were used to investigate the electronic structure & broadband molar absorption of synthesized duplex DNA oligonucleotides with designated stacking sequence and human telomere G-quadruplex DNA molecules. The optical absorption features in UV-Vis wavelength range were correlated with interband transitions in between the functional groups consisting DNA molecules. This study includes two aspects: 1: Duplex DNA molecules with sequence (AT)10, (AT)5(GC)5, (AT-GC)5, (AT)5(CG)5 and (AT-CG)5 were used to reveal the effect of the composition, stacking sequence, and polarizability distribution of the nucleotides on the optical properties and electronic structures of DNA; 2. Quadruple structured DNA d[AG3(TTAG3)3] and a duplex DNA composed of d[AG3(TTAG3)3] and its complementary strand d[TC3(AATC3)3] were measured to reveal the relationship between optical properties and morphology.

It was concluded that the relative strength of 229 nm & 260 nm absorption peak, the overall UV-Vis absorption intensity, and the absorption edge onset provide useful metric for the content and distribution of nitrogen bases on duplex DNA; G-quadruplex DNA samples show characteristic straight absorption edge and flat-roof predominant absorption peak. These results highlight the benefit of full spectral analysis of DNA, as opposed to reductive methods that consider only the absorption coefficient at 260 nm, 230 nm and 280 nm.

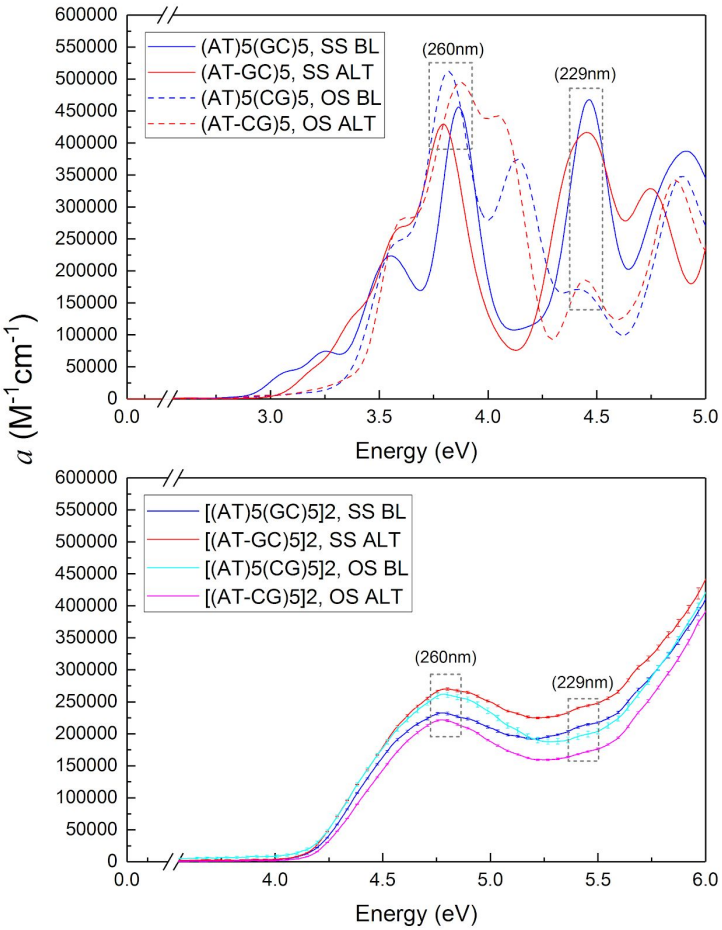

Fig. 3 Decadic molar absorption coefficient of four duplex DNA oligonucleotides determined from ab initio calculation and optical absorption measurement

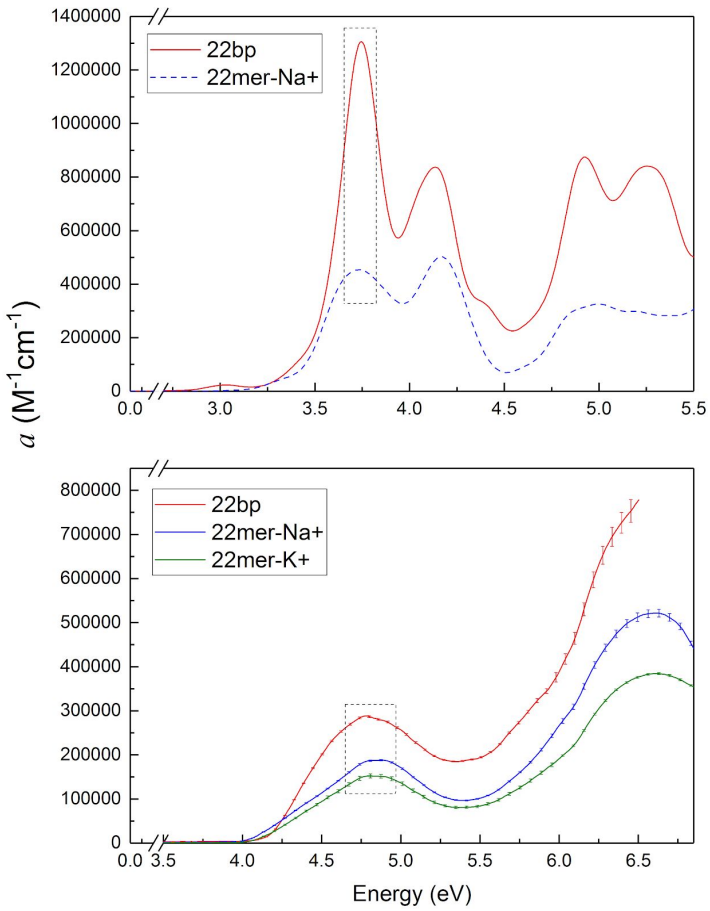

Fig. 4 Decadic molar absorption coefficient of G-quadruplex DNA d[AG3(TTAG3)3] in sodium phosphate and potassium phosphate solution and the corresponding duplex DNA

1e) Electronic Structure, Dielectric Response and Surface Charge Distribution of RGD (1FUV) Peptide (UMass, CWRU, UMKC)

Long- and short-range molecular interactions govern molecular recognition and self-assembly of biological macromolecules. We report a *one-swoop-methodology* for the *ab initio* quantum mechanical (QM) calculations that yields the partial charges as well as the frequency-dependent dielectric response function, that can then be taken as input for macroscopic theories of intermolecular forces. We apply this methodology to obtain the electronic structure of the cyclic tripeptide RGD-4C.

We have studied the electronic structure, partial surface charge distribution (see Fig.) and imaginary part of the frequency-dependent dielectric response function in the RGD-4C peptide, specifically for the RGD-A isomer (1FUV), based on rigorous *ab initio* QM calculations. By resolving the total density of states of the peptide into contributions from individual amino acids, detailed interactions between them at an atomic level can be further elaborated. The surface charge density and the polarity distribution show that the molecule is able to promote interactions with its $\alpha_v\beta_3$ integrin receptor either via long-range electrostatic complementarity or short-range hydrogen bonding.

The optical properties of this peptide show a striking feature of two sharp absorption peaks apart from the bulk broad interatomic bonding peak. It is conceivable that the unique optical

spectrum of RGD peptide could result in a strong vdW-Ld attractive force that could influence their interactions with other molecular moieties and modify its mobility in the aqueous solution.

1f) DNA/Doxorubicin Solvation and Binding (UMass, CWRU, UMKC)

The electronic structure and partial charge of doxorubicin (DOX) in three different molecular environments - isolated, solvated, and intercalated in a DNA complex—are studied by first-principles density functional methods. It is shown that the addition of solvating water molecules to DOX, together with the proximity to and interaction with DNA, has a significant impact on the electronic structure as well as on the partial charge distribution. Significant improvement in estimating the DOX–DNA interaction energy is achieved. The results are elucidated by resolving the total density of states and surface charge density into different functional groups. It is concluded that the presence of the solvent and the details of the interaction geometry matter greatly in determining the stability of DOX complexation. Ab initio calculations on realistic models are an important step toward an accurate description of the interactions in biomolecular systems.

2. Intermolecular interactions determined by static light scattering studies

Composition-gradient multi-angle static light scattering (CG-MALS) is an emerging technique in the measurement of intermolecular interactions. With CG-MALS, detailed studies of second virial coefficient (B22) can be carried out more accurately and effectively than with traditional spectroscopic methods.

2a) Second Virial Coefficient of Bovine Serum Albumin as a Function of pH and Ionic Condition (CWRU, UMKC)

We measure the B22 of bovine serum albumin (BSA) in aqueous solutions at various pH and ionic strength of the univalent salt (NaCl) solution. The magnitude of B22 shows systematic variation as a function of pH and NaCl strength, which reveals net charge change and the isoelectric point of BSA under different conditions. The magnitude of B22 decreases to 1.13 x 10^{-5} ml*mol/g^2 near the isoelectric point at pH of 3.92 and 25 mM NaCl. These results illuminate the significant role of electrostatic and van der Waals forces, and pH and ionic strength, in protein self-interaction. This experimental technique opens up the opportunity for direct and detailed studies of the fundamental long range interactions.

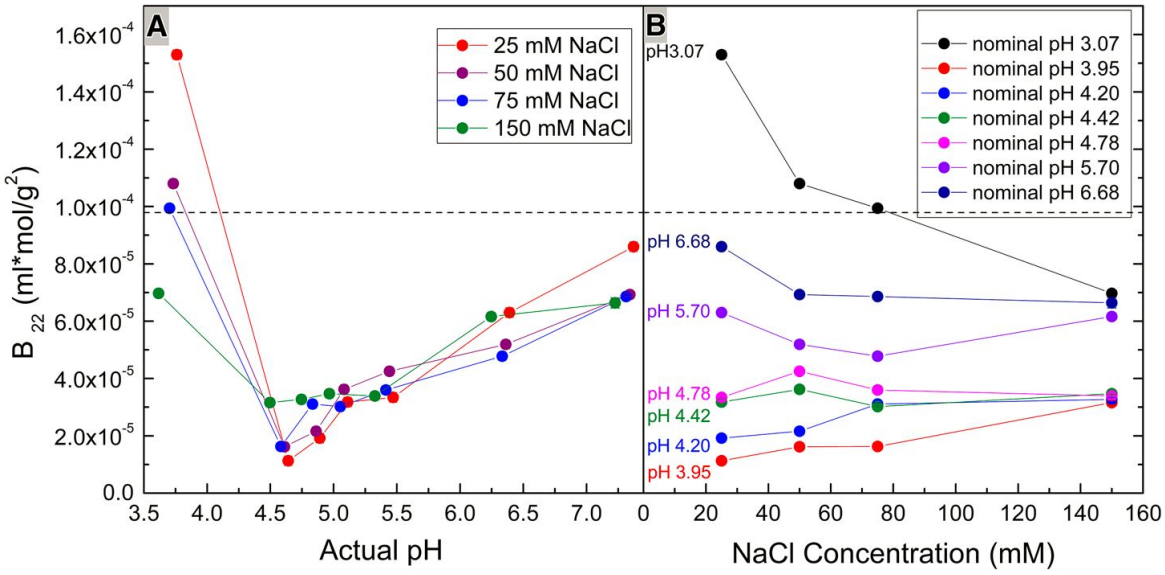

Fig. 5 Variation of the second virial coefficient as a function of the pH and the ionic strength of the NaCl.

2b) Intermolecular Interactions of Duplex vs. G-quadruplex DNA (CWRU)

The second virial coefficient of G-quadruplex DNA d[AG3(TTAG3)3] in sodium phosphate solution and potassium phosphate solution, and duplex DNA composed of strand d[AG3(TTAG3)3] and d[TC3(AATC3)3] are characterized from pH 7 to 5. The variation of B22 as a function of pH reveals the ionization and protonation behaviors of unpaired nitrogen bases in G-quadruplex, and the denaturation of duplex DNA at acidic environment.

2c) Second Virial Coefficient of Native and PEGylated Cowpea Mosaic Virus (one journal article in preparation) (CWRU)

Cowpea mosaic virus (CPMV) is a ~30 nm sized icosahedral nanoparticle consisting of a protein shell and an RNA-containing cavity. The surface property of the virus could be altered by chemical conjugation. With well-defined structure, good thermal and chemical stability, and mature replication and purification techniques, CPMV has become a proming building block for supramolecular arrays. In order to understand the self-interactions between native CPMV particles and effect of PEGylation on CPMV, we measured the second virial coefficient of CPMV and CPMV-PEG2000 at several pH conditions between pH 7.5 and pH 4.2. As the pH decreases, the CPMV solution exhibits lower stability associated with net repulsion-to-attraction conversion of intermolecular forces. In the case of CPMV-PEG2000, the conjugated PEGs introduce an additional steric repulsion and enhances the stability of the solution. This study could serve as a reference for the future construction of CPMV and PEGylated CPMV-based supramolecular self-assemblies.

3. Implement new numerical solutions of vdW interaction potential into Gecko Hamaker program

3a) Gecko Hamaker open source platform: development of the vdW-Ld tool (CWRU)

The ability to design and control the assembly and temporal evolution of nano- and meso-scale systems presents a critical challenge to scientists across a range of disciplines and technologies, including colloids, magnetic nanoparticles, and biomaterials. Universal to all these systems are the van der Waals-London dispersion (vdW-Ld) interactions, which arise from the spontaneous fluctuations of dipoles across interfaces between optically disparate media. These forces, despite their ubiquity, are often ignored or crudely approximated due to the lack of full spectral optical properties for the constituent materials or the perceived difficulty of implementing the full solutions. However, the availability of new optical property spectra (both experimental and ab initio) along with newly derived, fully retarded solutions to the Lifshitz formulations for a range of new system geometries such as optical anisotropic cylinders, have facilitated the implementation of an open-source, open-data design tool that renders tractable both an understanding and a predictive design capability for vdW-Ld interactions in a wide variety of critical contexts. The Gecko Hamaker open-source software project provides a database of spectral optical properties of materials, along with the fully retarded Lifshitz formulations for isotropic and anisotropic plane-plane, plane-cylinder, and cylinder-cylinder interactions in all cases with intervening inter-layer materials. It also models planar systems of up to 99 layers, including graded interfaces such as grain boundaries. The software and source code are distributed freely on Sourceforge and the up-to-date spectral optical property database is available as a web-service providing machine-readable optical property data. This makes Gecko Hamaker broadly available to both specialists focused on long range interactions and to nonspecialists who are focused on advanced designs for new applications, and technologies, in energy, chemistry, physics and biology, so that they may benefit from the advances in our scientific understanding of long range interactions and the vdW-Ld interactions in particular for mesoscale science.

3b) Long range interactions and design rules for nanoengineering (CWRU)

Long-range interactions play a critical role in nanoscale assembly and disassembly of biomolecular and inorganic materials systems, including proteins such as collagen and viruses. In the case of viruses and viral nano-particles we have summarized a set of design rules, based in our understanding of the role and dependence of the long-range interactions active in these macromolecular structures.

3c) Long-range interactions in Coulomb fluids (UMass)

We wrote a review on the current state of statistical mechanics of Coulomb fluids with special emphasis on the long-range interactions between charged macromolecular surfaces where the role of Coulomb interactions can be so drastic that, as evidenced by numerous experimental and theoretical investigations over the last several years, it can challenge our understanding of electrostatic effects as demonstrated by non-conventional phenomena such as electrostatic attraction between like-charged surfaces that are highly relevant in many experimental situations especially in (bio)materials and energy materials science.

4. Develop LRI-driven self-assembly for energy harvesting application (CWRU)

As the final step of the project, we explored the creation of light capturing nanostructures through LRI-driven bottom-up self-assembling approach. CPMV particles (negatively charged)

and positively charged dendrimer polymers were alternatively deposited on a gold substrate to form a family of semi-ordered multilayer structures. Spectroscopic measurements demonstrated broadband low-angular dependent antireflection properties of the self-assembled structure; a 46% and 43% reduction for S-polarized and P-polarized specular reflection are observed at 400 nm, and a 25% enhancement of transmission is detected at 535 nm. The mechanisms of light-matter interaction was revealed by computational optics modeling. It is noted that this type of self-assemble structure could be deposited on other substrates, and the antireflection and light trapping efficiency may be improved by incorporating inorganic matter. This study highlights the significance of the whole project and opens up the bioengineering approach for constructing self-assembled structure for light management.

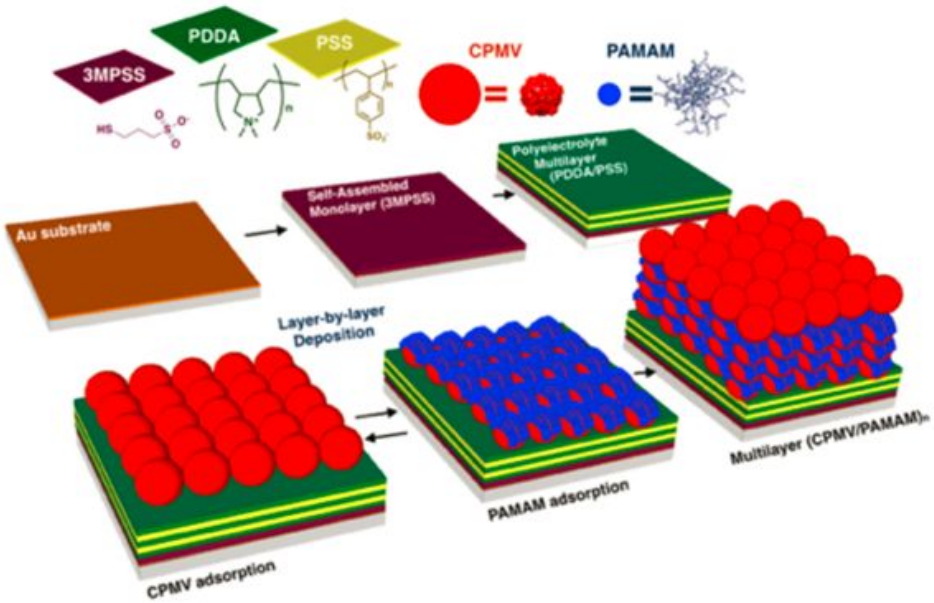

Fig. 6 Cartoon showing layer-by-layer deposition of CPMV and PAMAM (dendrimer) assembly on gold substrate..

IV. Publications

Published papers:

1. Rick F. Rajter, Roger H. French, W. Y. Ching, Rudolf Podgornik & V. Adrian Parsegian. Chirality-dependent properties of carbon nanotubes: electronic structure, optical dispersion properties, Hamaker coefficients and van der Waals-London dispersion interactions. RSC Adv. 823–842 (2013). doi:10.1039/C2RA20083J
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2. Badasyan, A., Tonoyan, S., Giacometti, A., Podgornik, R., Parsegian, V.A., Mamasakhlisov, Y., and Morozov, V. Osmotic Pressure Induced Coupling between

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3. Rudolf Podgornik, Jaime Hopkins, V. Adrian Parsegian, and Murugappan Muthukumar. Polymers Pushing Polymers: Polymer Mixtures in Thermodynamic Equilibrium with a Pore. Macromol. 45 8921 (2012).
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4. Ali Naji, Matej Kanduc, Jan Forsman, and Rudolf Podgornik, Perspective: Coulomb fluids—Weak coupling, strong coupling, in between and beyond, , J. Chem. Phys. 139, 150901 (2013).
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5. Jaime C. Hopkins, Daniel M. Dryden, Wai-Yim Ching, Roger H. French, V. Adrian Parsegian, Rudolf Podgornik, Dielectric response variation and the strength of van der Waals interactions, Journal of Colloid and Interface Science 417 278–284 (2014).
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6. Yasar, S., Podgornik, R., Valle-Orero, J., Johnson, M. R. & Parsegian, V. A. Continuity of states between the cholesteric → line hexatic transition and the condensation transition in DNA solutions. Scientific Reports 4, 6877 (2014).
   DOE support is acknowledged: This research was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering under Award DE-SC0008176.
7. Amy M Wen, Pooja H Rambhia, Roger H French, Nicole F Steinmetz, “Design rules for nanomedical engineering: from physical virology to the applications of virus-based materials in medicine” Journal of biological physics, 39, 2, 301-325, 2013.
   DOE Support Acknowledged: “This work was supported by NIH/NIBIB grant R00 EB009105 (to NFS, for the contribution on virus-based nanomedicines and identification of design rules), NIH/NIBIB training grant T32 EB007509 (to AMW, for the contribution on virus-based nanomedicines), Mt. Sinai Foundation (to NFS, for the contribution on virus-based nanomedicines and identification of design rules), and DOE-BESDMSE-BMM under award DE-SC0008068 (to RHF, for the contribution of role of long range interactions in self-assembly)”
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9. Neng Li and W.Y. Ching, “Structural, electronic and optical properties of a large random network model of amorphous SiO_2 glass”, J. Non-crystalline Solids. 383 (2014) 28–32.
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10. Daniel M. Dryden, Guolong L. Tan & Roger H. French. Optical Properties and van der Waals–London Dispersion Interactions in Berlinite Aluminum Phosphate from Vacuum Ultraviolet Spectroscopy. J. Am. Ceram. Soc. 97, 1143–1150 (2014).
    DOE support is acknowledged: “We are grateful to Dr. L. K. Denoyer for software development and M. K. Yang for help with the spectroscopy. This work was funded by DOE-BES-DMSE-BMM under award DE-SC0008068.”
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13. Rikkert J. Nap, Anže Lošdorfer Božič, Igal Szleifer, and Rudolf Podgornik. The Role of Solution Conditions in the Bacteriophage PP7 Capsid Charge Regulation. Biophysical Journal **107,** 1970-1979 (2014).
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    for many discussions regarding fundamental problems in viral nanoparticle assembly.
    A.L.B. acknowledges support by Slovene Agency for Research and Development through grants No. P1-0055 and J1-4297. R.P. acknowledges support in the study of long-range interactions for biomolecular and inorganic nanoscale assembly by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering
    under award No. DE-SC0008176. I.S. acknowledges support from National Science Foundation grant No. CBET-1403058.”
14. P. Adhikari, A. M. Wen, R. H. French, V. A. Parsegian, N. F. Steinmetz, R. Podgornik, and W.Y. Ching. Electronic Structure, Dielectric Response, and Surface Charge Distribution of RGD (1FUV) Peptide. Scientific Reports **4,** 5605 (2014).

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15. Yingfang Ma, Diana M. Acosta, Jon R.Whitney, Rudolf Podgornik, Nicole F. Steinmetz, Roger H. French, V. Adrian Parsegian. Determination of the second virial coefficient of bovine serum albumin under varying pH and ionic strength by composition-gradient multi-angle static light scattering. J Biol Phys 41, 85–97 (2015).
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17. Jacob. B. Schimelman, Daniel. M. Dryden, Lokendra Poudel, Katherine E. Krawiec, Yingfang Ma, Rudolf Podgornik, V. Adrian Parsegian, Linda K. Denoyer, Wai-Yim Ching, Nicole F. Steinmetz, and Roger H. French. Optical properties and electronic transitions of DNA oligonucleotides as a function of composition and stacking sequence. Physical Chemistry Chemical Physics 17, 4589–4599 (2015).
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Papers to be submitted:

1. Ma, Y., Nguyen, T., George, J., Poudel, L., Parsegian, V. A., Podgornik, R., Steinmetz, N. F., Ching, W.-Y. and French, R. H. Human telomere G-quadruplex and duplex DNA: electronic structure, optical properties and second virial coefficients. In Preparation, 2018. To be submitted to Scientific Reports
2. Ma, Y., Schimelman, J. B., Poudel, L., Parsegian, V. A., Podgornik, R., Ching, W.-Y., Steinmetz, N. F. and French, R. H. The effect of base-pair polarizability and stacking sequence on the electronic structure and optical properties of duplex DNA. In Preparation, 2018. To be submitted to Physical Chemistry Chemical Physics
3. Ma, Y., Acosta, D. M., Parsegian, V. A., Podgornik, R., Steinmetz, N. F., and French, R. H. The second virial coefficient of native and PEGylated cowpea mosaic virus under varying pH conditions. In Preparation, 2018. To be submitted to Journal of Biological Physics.
4. Ma, Y., Tan, G., Ching, W.-Y. and French, R. H. Vacuum-ultraviolet optical properties and van der Waals interactions of 6H-SiC. In preparation, 2018. To be submitted to Journal of the American Ceramic Society

Conference papers

1. Daniel M. Dryden, Yingfang Ma, Jacob Schimelman, Diana Acosta, Lijia Liu, Ozan Akkus, Mousa Younesi, Islam Anowarul, Linda K. Denoyer, Wai-Yim Ching, Rudolf Podgornik, V. Adrian Parsegian, Nicole F. Steinmetz, Roger H. French. Optical

Properties and van der Waals-London Dispersion Interactions in Inorganic and Biomolecular Assemblies. in *MRS Proceedings* 1619, (2014).

DOE Support Acknowledged: "Work was supported by DOE-BES- DMSE-BMM under award DE-SC0008068 (experimental) and award DE-SC0008176 (theoretical)."

2. Selcuk Yasar, Rudolf Podgornik & V. Adrian Parsegian. Continuity of States in Cholesteric - Line Hexatic Transition in Univalent and Polyvalent Salt DNA Solutions. in *MRS Proceedings* 1619, (2014).

   DOE Support Acknowledged: "This research was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering under Award DE-SC0008176."

3. Jaime C. Hopkins, Daniel M. Dryden, Wai - Yim Ching, Roger H. French, V. Adrian Parsegian and Rudolf Podgornik. Dependence of the strength of van der Waals interactions on the details of the dielectric response variation. *MRS Online Proceedings Library Archive* 1648, (2014).

   DOE support is acknowledged: "This research was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering under Award DE-SC0008176 and DE- SC0008068. "

Book chapters:

1. Glidden, M.D., Edelbrock, J.F., Wen, A.M., Shukla, S., Ma, Y., French, R.H., Pokorski, J.K., Steinmetz, N.F. , Application of engineered viral nanoparticles in materials and medicine, in Chemoselective and Bioorthogonal Ligation Reactions: Concepts and Applications, 631–710 (Wiley-VCH Verlag GmbH & Co. KGaA, 2017). doi:10.1002/9783527683451.ch18

   DOE Support Acknowledged: "This work was supported by the following grants: NSF CMMI NM 333651 (to N.F.S., for the contribution on VNP/VLP production and modification), NSF CHEM MSN 1306447 (to J.K.P and N.F.S., for contribution on VNP/VLP polymer hybrids), and DOE--BES DMSE-BMM DE--SC0008068 (to R.H.F. and N.F. S.) for the contribution on materials science)."

V. Other Outreach and Presentation activities

1. JCP featured our paper "Perspective: Coulomb fluids -- weak coupling, strong coupling, in between and beyond" in of Vol. 139, Issue 15, 21 October 2013. As an *Editor's pick* the article Entered JCP Spotlight Collections and features an *interview* with R. Podgornik on the occasion of publication of this paper. The Editors of The Journal of Chemical Physics have also selected a few notable JCP articles that represent the most innovative and influential articles of 2013. Our article has been chosen to be included in the 2013 JCP *Editors' Choice collection*.
2. At the annual summer school "Soft Solids and Complex Fluids", University of Massachusetts, Physics Department, June 2013, R. Podgornik delivered a set of lectures on the physics of DNA where he specifically referred to the work in this DOE grant:

   - Podgornik, Rudolf. Physics of DNA : [invited lecture at the annual summer school Soft Solids and Complex Fluids, University of Massachusetts, Physics Department, June 3, 2013]. 2013.

- Podgornik, Rudolf. Physics of DNA : [invited lecture at the annual summer school Soft Solids and Complex Fluids, University of Massachusetts, Physics Department, June 4, 2013]. 2013.

- Podgornik, Rudolf. Physics of DNA : [invited lecture at the annual summer school Soft Solids and Complex Fluids, University of Massachusetts, Physics Department, June 5, 2013]. 2013.

- Podgornik, Rudolf. Physics of DNA : [invited lecture at the annual summer school Soft Solids and Complex Fluids, University of Massachusetts, Physics Department, June 6, 2013]. 2013.

3. Activities in August 2013:
   - Roger H. French, N. F. Steinmetz, Long Range van der Waals-London Dispersion Interactions for Biomolecular and Inorganic Nanoscale Assembly, DOE-BES-DMSE-BMM PIs Meeting, poster.

   - V. A. Parsegian, W. Y. Ching, Long Range van der Waals-London Dispersion Interactions for Biomolecular and Inorganic Nanoscale Assembly, DOE-BES-DMSE-BMM PIs Meeting, talk.

   - Roger H. French, From Quanta to the Continuum: Opportunities for Mesoscale Science, DOE-BES-DMSE-BMM PIs Meeting, talk.

4. Presentations in November 2013:

   - Daniel M. Dryden, Yingfang Ma, Jacob Schimelman, Diana Acosta, Lijia Liu, Ozan Akkus, Mousa Younesi, Islam Anowarul, Linda K. Denoyer, Wai-Yim Ching, Rudolf Podgornik, V. Adrian Parsegian, Nicole F. Steinmetz, Roger H. French, “Optical Properties and van der Waals-London Dispersion Interactions in Inorganic and Biomolecular Assemblies”, MRS Fall Meeting 2013 presentation.

   - Jaime C. Hopkins, Daniel M. Dryden, Wai - Yim Ching, Roger H. French, V. Adrian Parsegian, Rudolf Podgornik “Dielectric Response Variation and the Strength of van der Waals Interactions “, MRS Fall 2013 Meeting presentation.
   Selcuk, Yasar, Rudolf Podgornik, V. Adrian Parsgiean, "Continuity of States in Cholesteric - Line Hexatic Transition in Univalent and Polyvalent Salt DNA Solutions"", MRS Fall Meeting 2013 presentation.

5. Activities in December 2013:
   - Ching, Wai-Yim. Application of the orthogonalized linear combination of atomic orbital method to complex materials. John H. Van Vleck Lecture, University of Wisconsin-Madison, 3-27,2014.
   - Diana Acosta, Yinfang Ma, Roger H. French, Second virial coefficients of Proteins and their Dependence on Ionic Strength and pH, Case Research Intersections, undergraduate research poster.
   - R. Podgornik was a visiting professor at the *Technische Universitaet Berlin* and the *Freie Universitaet Berlin*, where he delivered a set of lectures where he specifically referred to the work performed under this DOE grant:
   - Podgornik, Rudolf. Disorder and Coulomb interactions : [invited colloquium at Technische Universität Berlin, Eugene Wigner Colloquium, 5. 12. 2013].
   - Podgornik, Rudolf. DNA-protein interactions in virus-like nano-particles : [colloquium at Freie Universität Berlin, SFB 1112-Colloquium, 12. 12. 2013].

- Podgornik, Rudolf. Kirkwood-Schumaker forces and monopolar thermal Casimir interactions : [invited lecture at the Institut für Theoretische Physik, Freie Universität Berlin, 13. 11. 2013].
- Podgornik, Rudolf. Long-range interactions between DNA molecules : [invited lecture at Technische Universität Berlin, 14. 11. 2013].
- Podgornik, Rudolf. The nature and characterization of order in high density DNA mesophases : [invited lecture at Technische Universität Berlin, 15. 11. 2013].

6. Poster in April 2014:
   Yingfang Ma, Diana Acosta, Daniel Dryden, Jacob Schimelman, Roger H. French, "Optical Properties and Long Range Interactions in Biomolecular Assemblies" Case Research Showcase, Cleveland.
7. Poster in October 2014:
   - Acosta, D. M., Ma, Y., Wen, A., Podgornik, R., Parsegian, V. A., French, R. H., and Steinmetz, N. F. Study of the Second Virial Coefficient of Cowpea Mosaic Virus Under Varying pH and Ionic Strength Using Composition-Gradient Multi-Angle Light Scattering. 2014 Biomedical Engineering Society Annual Meeting. San Antonio, TX.
   - Krawiec, K., Lee, K., Dryden, D. M., Ma, Y., French, R. H., Steinmetz, N. F., Poudel, L., Ching, W.-Y., Podgornik, R., and Parsegian, V. A. Experimental Optical Properties Of Quadruplex DNA. 2014 Biomedical Engineering Society Annual Meeting. San Antonio, TX.
8. Activities in December 2014:
   - Ma, Y., Acosta, D. M., Wen, A., Whitney, J. R., Podgornik, R., Steinmetz, N. F., Parsegian, V. A., and French, R. H. Characterization of Long Range Interactions Between Nano Particles via the Second Virial Coecient As a Function of pH and Ionic Strength. 2014 Materials Research Society Fall Meeting presentation. Boston, MA.
   - J.C. Hopkins, D.M. Dryden, L.K. Denoyer, L. Poudel, N.F. Steinmetz, W. Ching, R. Podgornik, V.A. Parsegian, and R.H. French. Gecko Hamaker: An Open Source Tool for the Mesoscale Science. 2014 Materials Research Society Fall Meeting poster. Boston, MA.
9. Poster in October 2016
   George, J. R., \textbf{Ma, Y.}, and French, R. H. Long Range Interactions and Second Virial Coefficients of Duplex and Quadruplex Human DNA. 6th Annual Biomaterials Day, Case Western Reserve University. Cleveland, OH. Oct. 15th, 2016.

VI. Database and Software, and the websites that reflect the results

New LRIs solutions were implemented into Gecko Hamaker program (as illustrated in Section 3a) of Facts, figures, analyses used during the life of the project to support the conclusions and the 24th Published paper listed above), and the database of the program was enlarged and hosted by Case Western Reserve University.
The Gecko Hamaker program is open-source. The executable code, user documentation and developer documentation are publicly downloadable through the Sourceforge webpage: http://geckoproj.sourceforge.net/

VII. Networks and collaborations fostered

1. We collaborated with Prof. Ozan Akkus's group (Dept. of Mechanical and Aerospace Engineering, Case Western Reserve University) in the preparation and optical

characterization of type I collagen film. The research accomplishment was illustrated in the first Conference paper listed above.

2. The collaboration with Dr. Benjamin Gilbert (a Staff Scientist in Energy Geosciences Division of Lawrence Berkeley National Laboratory) was initiated.

VIII. Computer modeling

Computational optics modeling was used to simulate the interaction between visible-NIR light and biopolymer-based energy harvesting self-assembled nanostructure (as summarized in Section 4 of Facts, figures, analyses used during the life of the project to support the conclusions).

The underlying principle of light-matter interaction was Maxwell's equations, the well-acknowledged classical theory of electromagnetism. The program used to solve the light-matter interaction problem was EMFlex, a finite-element time domain program. This program generates solutions by minimizing the error in the integral form of Maxwell's equations (as shown below) over the computational domain.

$$\oiint_{\partial\Omega} \mathbf{D} \cdot \mathrm{d}\mathbf{S} = \iiint_{\Omega} \rho_{\mathrm{f}} \, \mathrm{d}V$$
$$\oiint_{\partial\Omega} \mathbf{B} \cdot \mathrm{d}\mathbf{S} = 0$$
$$\oint_{\partial\Sigma} \mathbf{E} \cdot \mathrm{d}\boldsymbol{\ell} = -\frac{d}{dt} \iint_{\Sigma} \mathbf{B} \cdot \mathrm{d}\mathbf{S}$$
$$\oint_{\partial\Sigma} \mathbf{H} \cdot \mathrm{d}\boldsymbol{\ell} = \iint_{\Sigma} \mathbf{J}_{\mathrm{f}} \cdot \mathrm{d}\mathbf{S} + \frac{d}{dt} \iint_{\Sigma} \mathbf{D} \cdot \mathrm{d}\mathbf{S}$$

Integral form of Maxwell's equations (https://en.wikipedia.org/wiki/Maxwell%27s_equations)

The model, assumptions, computing procedures and results, and the theory of light trapping behind the model have been described in the 25th Published paper listed above.