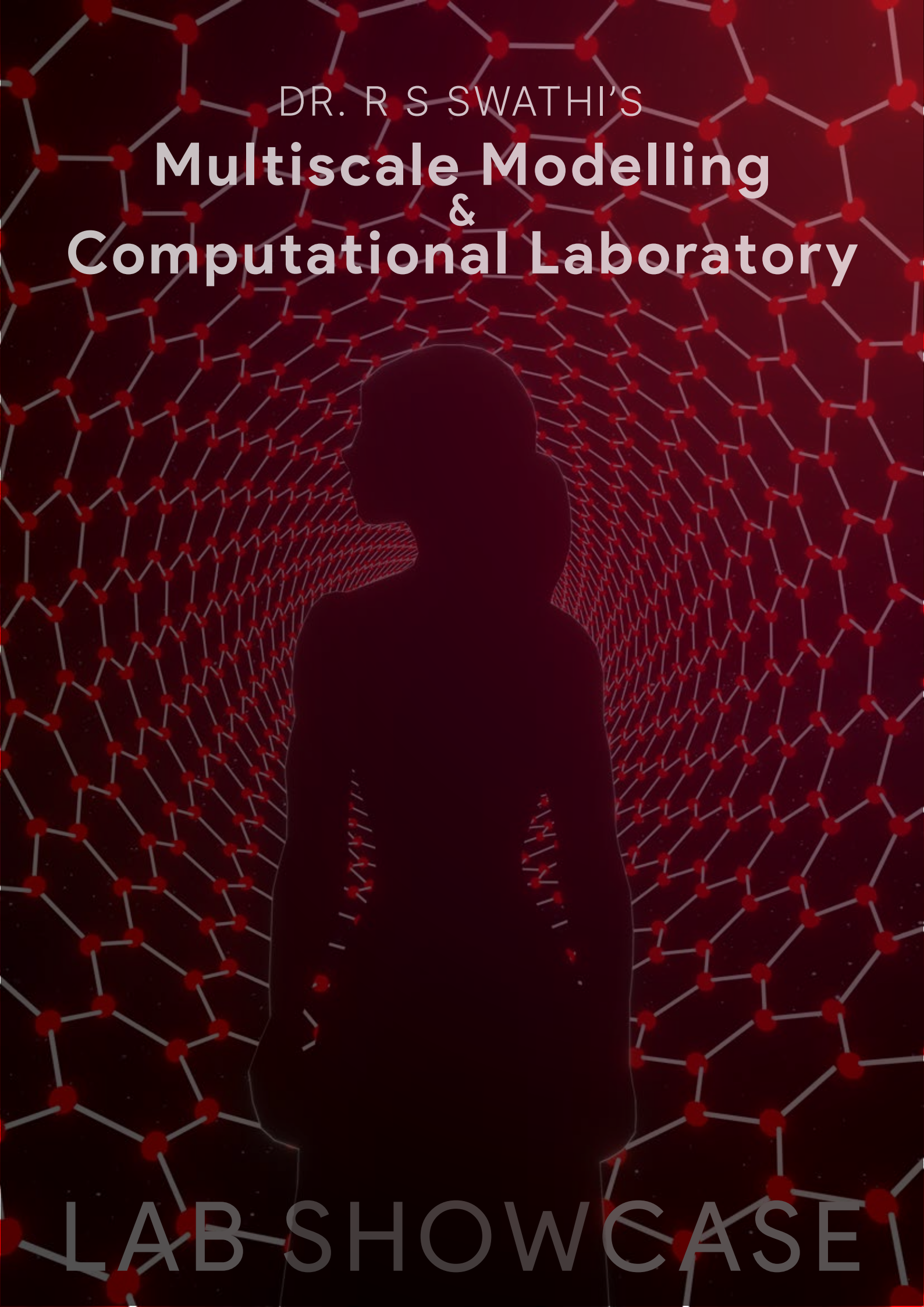
DR. R S SWATHI'S

Multiscale Modelling & Computational Laboratory



LAB SHOWCASE

Dr. R S Swathi's Multiscale Modelling & Computational Laboratory

The lab showcase is a novel feature of our magazine wherein we learn about the research areas of our faculty and their laboratory environment to equip students with a better understanding of how research laboratories function.

Through the interview, we try to get a bird's eye view of our professors' research and explain lab techniques and instruments commonly used while working in their fields. We also get to learn about our professors'experiences and learn about how to work well in a research environment.

For the second installment of the series, Associate Professor **Dr R. S. Swathi** from the Indian Institute of Science Education and Research's School of Chemistry was interviewed by Sharika Ramesh, Nivedha Baskaran and Malavika Devi of BS-MS Batch 22 on behalf of CSIT on the 23rd of May, 2023.

Biography,

Dr. R. S. Swathi is presently working in Theoretical Chemistry, specifically in the area of modeling carbon and metal nanostructures using various computational techniques based on classical and quantum mechanical principles. Dr. Swathi obtained an integrated B. Sc. Ed (Physics, Chemistry, Mathematics) (1999-2003) degree from the Regional Institute of Education, Mysore, Karnataka, India. Following this, she obtained an M. Sc. in Chemistry (2003-2005) from the Indian Institute of Technology, Guwahati, Assam, India. She pursued her PhD (2005 - 2010) at the Indian Institute of Science's Department of Inorganic and Physical Chemistry under Prof. K. L. Sebastian's guidance. She is currently working as an Associate Professor at IISER TVM's School of Chemistry and is the Principal Investigator of Swathi's Multiscale Modeling and Computational Group.

CSIT: *Thank you, ma'am, for taking time out of your schedule for this interview. We'd like to start by asking you to take us through your area of work.*

Dr Swathi: Our group at IISER TVM has been pursuing modeling and computational research on two major themes. The first theme pertains to carbon-based nanostructures, wherein we explore applications of carbon nanomaterials such as pristine and porous graphene, carbon nanotubes (CNTs), and fullerenes for sensing, storage and separation applications. We also work with an interesting class of novel 2D membranes called graphynes, which have been synthesised very recently, to probe sieving and separation applications. As a part of investigating the applications of these materials, we develop empirical intermolecular potentials, where a lot of cost-cutting of computational efforts come into play. We develop methodologies that can give results in reasonable computational times than what conventional first-principles approaches would provide. Of course, there is a compromise on the accuracy of the calculations, but theorists often resort to various approximations to improve the accuracy of various calculations and attempt to bring down computational costs so that we can model realistic systems in reasonable computational times. This is one key aspect of carbon-based nanostructures that we are working on.

The second theme of our research focuses on modeling plasmonic nanostructures for spectroscopic applications. Here, we predict the spectroscopic properties of metallic nanostructures. When metal particles come together, there are intense electric fields that are created at their junctions upon optical excitation, which have great relevance for single-molecule spectroscopy. Our group's interest has been in modeling the optical features of plasmonic nanostructures. We resort to approximate methodologies like quasi-static approximation and coupled dipole approximation. These are our favourites in plasmonic nanostructure modeling, but we also employ benchmarks to develop our methodologies, and the benchmark computational methodology that we use in plasmonic simulations is the finite-difference time-domain (FDTD) method. Likewise, in the context of modeling carbon nanostructures, about which we discussed earlier, we employ high-level electronic structure calculations that serve as benchmarks to develop empirical intermolecular pair potentials.

CSIT: *Could you elaborate on the types of approximations you use, the quasi-static and coupled dipole approximation?*

Dr Swathi: Sure. We resort to these approximations, as I said, with the primary objective of cutting down computational costs. When we want to, for example, model a metal particle's optical features, the quasi-static approximation enables modeling the optical features within a few seconds. It is an approximation in which Maxwell's equations that describe the interaction of light with the nanostructure are solved within a static framework. In principle, if one were to get exact solutions, one has to solve time-dependent Maxwell's equations in full space and time domains, and this is quite elaborate computationally. Therefore, we resort to the quasi-static approximation so that we can get the results in a few seconds. This is not too bad because this approximation enables us to calculate spectral features that are in fair agreement with what one would measure in experiments.

The coupled dipole approximation arises when one deals with interactions between metal nanostructures. When the distance between the particles is large enough compared to their sizes, one can treat the optical excitations in each of these nanostructures within a dipolar approximation and then the interactions between the two particles are described using a coupled dipole framework.

In the context of modeling carbon-based systems, we resort to what is known as a continuum approximation. What we do here is that, a typical structure like graphene, for example, is modelled as a sheet with uniform surface density of carbon atoms. Likewise, a CNT, which is a rolled-up sheet of graphene, is modelled as a uniform density of carbon atoms that is confined to a cylindrical region. In the same way, if you think of a fullerene, you could model it as a uniform density of carbon atoms confined to a spherical region. Now, the advantage of such an approach is that it exploits the symmetry of the nanostructures, and therefore enables us to write closed-form analytic expressions which are easy to program on a computer. This approximation works reasonably well in several contexts. Of course, one has to be careful in choosing the context in which one would like to use such approximations.

CSIT: *While modeling, you use classical and quantum mechanical methods. Could you tell us the pros and cons of each and how you would decide what to use in a particular experiment?*

Dr Swathi: It all depends on the problem that we have to model. Obviously, in principle, one would want to get highly accurate results, but most often, this comes with an extra computational cost. Therefore, in certain contexts, it suffices to work with classical approaches, while in certain others, quantum approaches do become imperative.

Let me give you an example from our own research, where we look at separating various chemical species using nanoporous membranes. There are various sieving mechanisms that are known. One is classical sieving, where if you have two gas particles, A and B, that are different in size, depending on their sizes and the pore that present in a nanoporous material, you can achieve sieving of these particles. All that you need is a classical kinetic theory of gases kind of formalism where you estimate the kinetic diameters of the gaseous particles A and B that you wish to separate. You also estimate the size of the nanoporous graphene membrane, and that suffices to predict whether the pore is able to sieve the two particles or not, within a classical framework.

Now, think of a similar context where we wish to separate two isotopes, for example, Helium-3 and Helium-4. There is no classical approach that you can use to achieve the separation or to describe the selective permeation of these isotopic species through carbon membranes. The mechanism that governs such a separation is what is refer to as quantum tunnelling. Now, in this context, there is no way that you can use a classical framework to model the separation of isotopes. Separating helium isotopes requires a fairly accurate quantum mechanical treatment. So, it really depends on the context at hand. Depending on the problem at hand, we choose the methodology that we want to resort to.

CSIT: *Could you elaborate on helium isotope separation and how it can be achieved using nanoporous graphene?*

Dr Swathi: Consider a classical particle encountering an energy barrier. If the energy of the particle is less than that of the barrier that it encounters, it cannot pass through the barrier. Similarly, if the particle has a greater energy than the barrier, it will certainly surmount the barrier. This means that the classical transmission probability is zero if the energy is less than the barrier, and it is one if the energy is greater than the barrier. Mathematically, the classical transmission probability is a step function. In quantum transmission, even if the particle has a lower energy than the barrier, there is a non-zero probability of it going through the barrier. Likewise, it has a non-zero probability of getting reflected back even if the energy that it possesses is higher than the barrier. The step function now modifies into a sigmoidal-type profile, and such a profile arises from quantum mechanical tunnelling. This quantum transmission propensity differs for Helium-3 and Helium-4 as it depends on the mass of the particle. This means that, at low temperatures where quantum effects become important, it is possible to separate the two isotopes using carbon membranes.

CSIT: *You must be using various software to perform the computations in your laboratory. Can you give us a brief overview of the software you use?*

Dr Swathi: As I said, our research primarily revolves around the modeling and computation of carbon-based and plasmonic nanostructures. In the case of carbon-based nanostructures, for the extensive benchmarking electronic structure calculations, we use the Gaussian software. In the case of modeling plasmonic nanostructures, we use FDTD simulations as the benchmarks and for this, we resort to a software called FDTD simulations, which is a product of Lumerical Ltd. based in Canada.

While we resort to the above-mentioned software with regard to benchmark computations, a lot of our studies are also based on in-house developed codes. In our analytical modeling methodologies based on continuum approximation, quasi-static approximation as well as empirical potential formulations, we develop codes in-house using Mathematica, Matlab and Python.

A lot of our current research interest also revolves around a swarm intelligence technique called particle swarm optimisation. All the codes pertaining to global optimisation techniques are also developed in-house.

CSIT: *Can you tell us a little more about FDTD?*

Dr Swathi: Yes. FDTD is a finite-difference time-domain technique, which has fairly broad applications, not just in the context of plasmonics. What it embodies is modeling the solutions to differential equations using finite-difference approaches. You are essentially solving the differential equations on a numerical grid of space and time. In fact, FDTD method is used in quantum mechanics for arriving at solutions to the Schrödinger equation.

CSIT: *Would you elaborate more on Swarm Intelligence?*

Dr Swathi: Sure. Swarm intelligence techniques are a class of techniques that fall under the general ambit of artificial intelligence. They are primarily motivated by natural phenomena such as the flocking of birds, fish schools and so on. Now, the philosophy of the particle swarm optimization (PSO), a swarm intelligence technique, is that you have a set of simple agents, and these agents interact with each other through intelligence. There are two major factors here. One is called a cognitive component, while the other is called a social component. The cognitive component pertains to the intelligence of the agent itself. The social component pertains to the intelligence of the swarm collectively. Now, imagine the motion of a collection of these agents. Their motion is guided by the exchange of information between them, in other words, by the cognitive as well as social components. The motion of the particles is also governed by stochastic rules. Typically, the stability of a chemical system is characterised by its energy. Lower the energy, higher is the stability. The potential energy surface of a chemical system is often very rugged, with various valleys, peaks and saddle points. Then, there is a global minimum, the lowest point on the potential energy surface, and this point corresponds to the lowest energy configuration of the chemical system, and therefore the most stable one. We essentially target reaching the global minima of the potential energy surfaces using global optimization techniques such as PSO.

Now, this is a complex optimization problem because you are looking at a multi-dimensional potential energy surface analysis. Deterministic techniques have their own limitations with regard to optimisation on these complex potential energy surfaces, necessitating the use of swarm intelligence techniques, which exploit the stochastic nature of the algorithm to quickly scan the potential energy surface and reach the global minimum.

CSIT: *So you chose graphene and CNTs as your area of research, and you mentioned the time when the possibilities of research in this field were immense. Could you please brief us on how this area has evolved through the years?*

Dr Swathi: As you all know, graphene was discovered in 2004, and the manner in which it was discovered made a rather strong revolution. The discovery was by the use of a simple scotch tape technique. You keep peeling layers off from graphite as they would peel off while writing with a pencil lead. As you keep peeling off layers, you will, at some point, end up with a single or a few layer graphene. The development of spectroscopic and microscopic characterisation techniques has enabled the discovery of a single layer of graphite, called graphene.

Now, the discovery of graphene was reported in 2004, and incidentally, I started my PhD in 2005. My supervisor was keen on modeling graphene-like systems for various applications, and he said to me: “Since you are interested in pursuing research on quantum approaches, why don't you try modeling the applications of graphene for energy transfer?”. That's how I got interested in the field, and I pursued part of my doctoral research on electronic excitation energy transfer to graphene.

With the discovery of graphene, numerous applications in electronics also opened up because of the exceptional band structure of graphene, which was considered very fanciful. Thus, after the discovery of graphene, we witnessed a lot of applications in electronics being reported, and I am sure there are far more waiting to be discovered.

CSIT: *Could you please explain how the band structure of graphene is unique?*

Dr Swathi: Conventionally, metals and semiconductors are understood in terms of their band structure. In the case of metals, there is an overlap between the valence and conduction bands. Similarly, in the case of semiconductors, there is a distinct and small gap between the valence and conduction bands. Graphene, however, is a zero-band gap semiconductor. A zero-band gap structure is characterised by the valence and conduction bands touching exactly at one point, and this point is referred to as a Dirac point. Now, because of the hexagonal symmetry of graphene, there are six such unique Dirac points in the band structure of graphene. A lot of interest in graphene for electronics-related applications comes from this band structure.

CSIT: *A lot of research into graphenes and graphynes seems highly futuristic. What are some applications of such materials that you are looking forward to in the future?*

Dr Swathi: When it comes to carbon nanostructures, it's a matter of pride for theorists that several predictions were made first in theory, and the experiments followed later. Graphene, after being discovered in 2004, immediately rose to prominence, and the period between 2004 to 2010 witnessed intense research activity on graphene. However, the theoretical approaches to model graphene date back to 1947! A famed theoretical physicist, P. R. Wallace, wanted to understand the band structure of graphite. Graphite, as you know, is a layered structure. He started with a single layer of graphite and derived the band structure of graphene way back in 1947. After the discovery of graphene, this paper started getting enormous attention. This is one instance in which theory preceded experiment. Yet another instance is in the context of graphynes, which were first predicted theoretically in 1987, while an experimental discovery came only in 2010!

Likewise, the saturated form of graphene, graphane, was also first predicted in theory! Graphane was theoretically predicted to have a stable structure that eventually was experimentally reported. Graphane can be obtained by saturating graphene with hydrogens.

We can see that, in a lot of these cases, theory has preceded experiments and the same, I would say, holds for applications. For example, one of the applications that I'm quite excited about is the application of nanoporous graphene for water purification in the form of reverse osmosis membranes. Desalination of water is an important fundamental and technologically relevant problem. Recently, there have been several studies suggesting that nanoporous graphene could be excellent reverse osmosis membranes. In fact, some technologies have already been developed based on nanoporous graphene. Theoretical studies have also reported that graphynes can be competitive, sometimes even superior to graphene, with regard to desalination applications. Another exciting future application for such materials lies in energy storage. We know that graphene has been an extremely popular material for electrode design in lithium-ion batteries. Graphynes have also shown competitive properties in this context. I believe that the future belongs to these membranes with regard to energy storage applications. Likewise, I talked about quantum sieving using nanoporous graphene. It should be possible in the future to achieve helium isotope separation and other quantum-sieving effects using such nanoporous materials. These are some applications that are, I'm sure, going to be realised in future!

Particularly because the synthesis of a variety of graphynes has been successfully reported in the past decade, I am looking forward to some of these applications being realized in experiments. It is also exciting that they might go on to become actual technologies.

CSIT: *What is the difference between using graphyne and graphene-based membranes?*

Dr Swathi: To begin with, the difference appears subtle; but the quantum transmission propensity depends very strongly on the nature of the membrane. Two pores with the same porous architecture but different atoms in the pore rings would make a great difference, as quantum tunnelling propensities in both the cases are very different.

Graphene, however, is not useful for any of these applications in its pristine form. It can be used for separation applications by drilling pores and obtaining nanoporous graphene. Graphynes, on the other hand, are built from molecular-level model systems. Their pores have various structures such as triangular, rhombi-like etc. As the pore architecture of nanoporous graphene and graphyne are different, their transmission probabilities also differ. Both these materials have their pros and cons. For example, creating a porous graphene membrane is easier when compared to the synthesis of graphynes. However, graphynes offer a uniformly porous architecture, while it is difficult to control the pore architecture of nanoporous graphene. Nonetheless, calculations have shown that both nanoporous graphene and graphynes are interesting substrates for isotope separation.

CSIT: *You have previously mentioned how, in your study of nanostructures, you compute many different parameters, such as intermolecular potential energy. How does something like intermolecular potential help in modeling a structure?*

Dr Swathi: We study the carbon-based nanostructures for sieving or separation and storage applications.

In the context of separation, we study the possibility of achieving atomic/molecular separation using nanoporous membranes. When we think of storage applications, we exploit the interior hollow spaces in fullerenes and CNTs to store atoms or molecules. At the fundamental level, if one were to model these applications, one needs to probe intermolecular interactions between these atomic/molecular species that bind to the carbon nanostructures. Such intermolecular interactions are what we represent by empirical force fields.

We have been interested in developing intermolecular force fields in the last few years. Intramolecular force fields are textbook examples in computational chemistry, as we have fairly developed our understanding of how to describe intramolecular interactions of chemical systems. However, intermolecular interactions, which are less studied, have very exciting manifestations and fundamental origins!

For example, we can consider dispersion interactions, cation-π interactions, anion-π interactions and π-π interactions, which are all extremely relevant today in the context of supramolecular chemistry. If one were to model large-scale systems involving such interactions, one must develop protocols for describing them! Here, we are developing intermolecular force fields to probe such interactions.

We thus compute the intermolecular potentials and develop force fields to understand how the molecules and materials interact with each other. We thereby predict the possible structures of chemical systems, along with their associated functional properties.

CSIT: *What drove you to pursue chemistry for your higher education and career?*

Dr Swathi: There were two main aspects that drove me to chemistry.

I pursued my undergraduate degree with physics, chemistry and mathematics as three primary and equally important subjects. I realised two things. Firstly, I was slightly better at chemistry than maths or physics, so I was more confident about taking it up! Secondly, I had an excellent teacher in physical chemistry who truly inspired me to pursue it further. In hindsight, I feel that the triple-major choice worked well for me as my research is in the area of theoretical chemistry, which is at the interface of the three disciplines, physics, chemistry and mathematics. If I were to think back, there is no way that I would have chosen anything else!

CSIT: *Being one of the top researchers in your field, at what point in your career did you feel like you finally made it?*

Dr Swathi: This, for me, is a tough question to answer! In my opinion, there have been phases of my career where I felt this. Let me illustrate this to you.

I joined IISER Thiruvananthapuram as a faculty member in 2010. Because of my former training with carbon-based nanomaterials, I started focusing on those materials. In the same year, the experimental synthesis of graphynes was reported for the first time.

I chanced upon a paper in which graphyne synthesis was experimentally reported, and I found its highly symmetric triangular porous structure very interesting. I felt that graphynes could be an excellent system to start working on. Hence, we began our research on exploring the properties and applications of graphynes. Following this, however, there was a lull period in this field. After the aforementioned publication in 2010, not many experimental reports pertaining to graphyne synthesis followed. We went ahead and performed several calculations on graphynes and reported some of our predictions. However, there was a point when there were apprehensions about whether graphynes could be made at a bulk scale in an accessible way and whether they really have any serious applications. In fact, at a conference, someone asked me if I was working theoretically on an almost unrealizable system! I was taken aback, to be honest, but it did not deter me because I had the conviction that they would soon be made at a bulk scale.

To my surprise, in the next 2-3 years, several papers came up synthetically reporting graphynes of various forms, using various solution-based methodologies! That was a point where we felt that the problems that we chose to work on were not trivial ones. Over time, our work on theoretical modeling of graphyne-based systems started drawing a good deal of attention from researchers elsewhere working on graphynes. I would say, that is one of the high points of my career because when the community acknowledges that what you have done is of some worth, that is a very gratifying moment!

The second high point of my career was when we started working on the swarm intelligence technique, PSO. It was not easy, as it required complex programming, and we needed to test out many ideas. My PhD student Owais started working on this and put in a lot of effort to develop the program codes. In this enterprise, there was more effort from his side than mine, to put it bluntly! We developed these codes over a period of four years. Another PhD student of mine, Chris, also worked with Owais and both their doctoral theses were submitted and evaluated by top scientists working on global optimisation. The examiners for both the theses were very appreciative of our work! This was greatly satisfying and was also one of the high points of my career because if our students are happy, then we are happy!

CSIT: *What advice do you have for us, as students, who will work in labs and start research work?*

Dr Swathi: There are three important factors that one has to bear in mind. The first is to get used to long working hours because research demands a lot of effort. Second is planning and management. There is no room for taking anything lightly, as time is crucial. The third is patience. Many a time you feel like you are not reaching where you want to be. It is easy to get dejected. One needs to put in conscious efforts to be patient. While pursuing my doctoral studies, concepts like CNTs and graphene were completely new, and I had no previous experience with programming as no conventional chemistry course offered a full-fledged programming course. So, one had to learn these aspects in informal settings to get on with one's research. There were points where I felt that I did not understand the band structures of graphene and CNTs. There were bugs in my programs which went unresolved for several months. My supervisor always believed in independent thinking and learning - it was okay to take months, but I had to sort out the problem myself. This has helped me a lot, but to be honest, there were points where I felt I was not going to make it. I realized that one must be patient and see-through; things will work out in the right way if one is perseverant.

CSIT: *We were huge fans of your course and your class. What's your approach to teaching? If you hadn't chosen research as your career, what do you think you would be doing right now?*

Dr Swathi: Teaching was always my first passion. I was not aware of research possibilities while I was pursuing undergraduate studies. My interest in teaching came from some of the kind teachers in Jawahar Navodaya Vidyalaya, Kurnool, where I had residential schooling. I went on to pursue undergraduate studies in a four-year integrated program, B.Sc. Ed. In addition to maths, physics and chemistry, we also had courses on psychology, philosophy of education and teaching methods. The B.Sc. Ed. program equips you with a bag of tricks that you can use in the classroom, and I try my best to use some of these. I will give an example.

There is a popular method called the whole-part-whole learning method in teaching methodologies. An effective method of education is that you first describe a problem as a whole, then in detailed parts and then describe it as a whole. It is the most effective mode of communication with students, and I follow the same while I teach. Because it is my first passion, there is no compromise. Every lecture is important and must be delivered with the same rigour.

If I were not a researcher, I would definitely have been a teacher!

CSIT: *Thank you, ma'am; this was indeed an inspiring session for us.*

Follow this QR to learn more about Dr. R S Swathi's Research Lab.