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Review Article

Statistical Mechanics in Theoretical Chemistry in India: Past, Present and A Bit of Future

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While the subject of statistical mechanics is intensely active in physics departments across India, with considerable activity even in mathematics departments, the same cannot be said for average chemistry departments in India where statistical mechanics is relatively less taught and even less pursued. This is to be contrasted with USA and many other developed countries (Germany, Israel) where statistical mechanics and spectroscopy are major disciplines in the physical chemistry departments. The situation, however, has changed rapidly in the past few decades. In this article we discuss the developments in this important area in the recent past, with emphasis both on analytical approach and those based on computer simulations. We also attempt to look into future problems where our efforts could be directed fruitfully.

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It is often said that chemistry means chemical reactions, and most of the chemical reactions occur in the solution phase. Many of the biochemical processes that sustain all forms of life occur in liquids or on surfaces. These systems are not only complex, the environment can be at best termed as random, although the randomness is often correlated. If we need to control the rate of such a reaction or the yield of the product, it is imperative to understand how these reactions occur and what factors control them.

Understanding reactions in solution or on surfaces however poses a serious problem because reactions occur, as mentioned above, in a dispersed medium and our control is often macroscopic, like concentration, viscosity, temperature or pH. At the same time, to control these reactions, we need to understand the underlying microscopic processes. The microscopic processes, like diffusion and activated barrier crossing dynamics are not deterministic, and one requires the use of the principles of statistical mechanics to obtain estimates of rate constant and of the yield. One needs to consider both equilibrium and time dependent aspects. For example, the synthesis of Zeolites and/or other such species by hydrothermal reactions, one can control the formation of the desired product by tuning the temperature and the concentration. Another example is the solvation properties of binary mixtures like water and ethanol. The properties of such mixtures depend critically on composition, and specific composition must be used in chemical synthesis. Yet another example comes from the dissociation of the hormone insulin from the dimer to monomeric form. This is an essential biochemical process important in our control of diabetes whose microscopic aspects are beginning to be addressed. There is of course the pressing issue of understanding the effects of chemotherapeutic drugs so routinely used in cancer often with strong side effects. The intercalation of these drugs into DNA is a subject of great importance. Clearly, the above list is endless. It is therefore not surprising that in many advanced countries physical chemists are working on understanding these problems. Along with quantum chemistry, a major tool one needs to use is statistical mechanics (Bagchi, 2018; Bagchi, 2012). Statistical mechanics can be broadly divided into two parts: Equilibrium and time dependent. *The latter is*

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the concern of the most of the physical chemists in India. However, implementation of the latter needs the former (Bagchi, 2018).

The development of statistical mechanics in chemistry in India has been slow. Physics had a head start in this area from the work of Professor Satyendranath Bose who pioneered Bose statistics (Bose, 1924). Prof. M N Saha, with Prof. Srivastava, wrote the influential text "Treatise on Heat" (Saha and Srivastava, 1958) that served as the introductory text to statistical mechanics for more than one generation of Indian scientists. The famous "Saha Ionization Theory" (Saha, 1920; Venkataraman, 1995) makes use of statistical mechanical concepts extensively.

Despite the remarkable interest in, and advances of, the subject among physicists, the same was almost completely lacking among chemistry students and graduates and researchers, till 1950s. Even Indian faculty members were largely unaware of the remarkable developments that were taking place in the use of statistical mechanics to the study of the problems of liquid phase chemistry, like electrochemistry (Debye and Onsager), phase transitions (Mayer's theory), polymer solutions (Flory), dipolar liquids (Debye, Onsager and Kirkwood), to name a few.

It could be said with fair amount of accuracy that the first applications to statistical mechanical concepts to physical chemistry was made by famous Professor Jnan Chandra Ghosh when he was a professor of Dhaka University of undivided Bengal. He developed a lattice model to explain certain anomalies observed in electrochemical conductance, and introduced the assumption of ion aggregation. His theory of ion association was one of the first theories of electrochemistry (Conway *et al*., 1983). The seminal works of Jnan Chandra Ghosh found praise from such scientists as G.N. Lewis, W.H. Nernst. Both mentioned Ghosh in their text books (Lewis and Randall, 1961; Nernst, 1895). Subsequently, statistical mechanics was used by Professor Sadhan Basu to study solvation of dipolar molecules in liquids and to find the dipole moment of the excited state. He used polymer distribution theory of viscosity to find the size of a DNA molecule in aqueous solutions (Basu, 1951). These were significant and path breaking contributions. Surprisingly, however, none of Professor Basu's students followed this branch of research.

After a lull of almost 20 years, studies of statistical mechanics in India was again initiated by Professor B L Tembe of IIT Bombay and Professor R Ramaswamy then at TIFR, Bombay, in 1980s (Tembe and Mozumder, 1983; Dhar and Ramaswamy, 1989). At that time, the theoretical physical chemistry was completely dominated by quantum chemists. The works of Professor Tembe and of Ramaswamy stood completely out of the main stream research in theoretical chemistry in 1980s.

At around the same time, a sustained and continued efforts to apply statistical mechanical methods to understand dynamics of dipolar liquids like water and acetonitrile (Bagchi, 2012) was initiated at the Indian Institute of Science, Bangalore. The theory was extensive and attracted considerable international attention. Among many novel results obtained, it will suffice to mention a few notable ones (Bagchi and Chandra, 1990; Bagchi and Chandra, 1991). (i) The molecular theory replaced the continuum model description by using two and three particle space and orientation dependent direct correlation functions. (ii) Derived molecular expressions for longitudinal and transverse dielectric functions. (iii) A microscopic theory of solvation dynamics was developed that stood the test of time. (iv) Many interesting phenomena, like Onsager's inverse snowball picture of polarization build-up around an ion, the hidden role of translational modes in dielectric friction, coupling between rotational and translational modes, and several others (Bagchi and Chandra, 1990; Bagchi and Chandra, 1991). The work was subsequently extended in many directions, including transport properties in electrolyte solutions (Chandra and Bagchi, 2000).

The period between 1990-2005 or so was particularly productive for statistical mechanics in chemistry in India. During this time, Prof. Swapan Ghosh and his team at BARC studied many aspects of phase transition, diffusion and electrical double layer formation (Samanta *et al*., 2001). At IISc, a theory was developed for "Biological Water" to explain biomolecular hydration dynamics (Nandi and Bagchi, 1997). A mode coupling theory was developed for diffusion and viscosity in binary mixtures (Mukherjee *et al*., 2002). At IIT Kanpur, a statistical mechanical

theory was developed by the group of Chandra to predict interfacial structure of dipolar liquids near solid surfaces which included the effects of quantum structure of free electrons in case of metals (Das *et al*.,1999). At IIT Delhi, the group of C Chakravarty developed statistical mechanical theory to study structure, delocalization and melting of quantum clusters and solids (Chakravarty 1995; Chakravarty and Linden-Bell 2000). Many interesting studies on statistical mechanics of polymers, complex condensed matter and electrochemical systems were also undertaken in IISc Bangalore, Delhi University and other places (Cherayil, 1997; Kant, 1993; Cherayil and Biswas, 1993). The same period also witnessed the beginning of simulations and theory of nematic liquid crystals. Studies on protein folding was also initiated. Important studies on such biochemical processes as drug-DNA intercalation, protein-DNA in teraction were also carried out. A statistical mechanical study of the role of vitamin D in human immunity was carried out that explores the interaction between pathogen antigen presenting cells, T-cells (or, killer cells) and vitamin D (Roy, 2014). As already mentioned, time dependent statistical mechanics is essential to understand spectroscopy, such as IR and Raman linewidths.

Because of the complexity and many-body nature of the systems involved, first principle statistical mechanical studies face an up-hill task when real systems are considered. For example, the properties of a dense liquid interacting with even a simple two-body radial potential cannot be solved rigorously to obtain many of the properties, without making approximations. Purely theoretical studies of the important liquid, water, remained out of bound despite many attempts. Help came in an unexpected way in 1950s when digital computers became available which could be used to solve Newton's equations numerically, and thus an initial state or configuration could be propagated through a series of discrete steps. Also, tools from the probability theory were implemented to generate random configurations of an equilibrium liquid, and average over such configurations allowed reliable calculation of such properties as the equation of state, phase transition parameters, diffusion coefficient and a host of other properties.

In 1964, a landmark paper (Rahman, 1964) in the area of computer simulations was published by Dr. A Rahman from Argonne National Laboratory who was a physicist from Hyderabad, India. This study opened the floodgate of simulation studies of liquids interacting with realistic potentials. In a series of papers, Rahman reported studies of many systems, including a celebrated study of water that formed the basis of many subsequent studies.

In 1980s, computer simulation studies of chemical systems also started in India in the groups of Prof. S Yashonath at IISc Bangalore and Prof. B L Tembe at IIT Bombay. In fact, the works of Prof. Yashonath was influenced greatly by Dr. A Rahman. One of the major outcomes of the simulation work in Prof. Yashonath's group was the so-called 'Levitation effect' where it was shown that a larger solute could pass through a narrow pore faster if certain subtle conditions were satisfied (Ghorai and Yashonath, 2005). Subsequently, such effect was also found to be present for diffusion of ions in water (Ghorai and Yashonath, 2006). Tembe's group came up with calculations of potential of mean force for various ion-ion, ion-solvent and solvent-solvent pairs from atomistic simulations (Madhusoodanan and Tembe, 1994; Das and Tembe, 1999). They estimated the relative stabilities of contact ion-pairs versus solvent separated ion pairs and other solvated ionic species in polar solvents. Prof. K L Sebastian (IISc.), Prof. D S Ray (IACS) and Prof. B Cherayil made important contributions on dynamics of chemical reactions. The reader is referred to their home pages for details of their work.

During 1995-2005 and onwards, several young physical chemists started working on statistical mechanics. They combined theory and simulations to produce important results. The groups of S Sastry and of S Balasubramanian at JNCASR, S Bandyopadhyay at IIT Kharagpur and C Mukhopadhyay at Calculatta University and also those of Bagchi at IISc Bangalore, Chandra at IIT Kanpur and Chakravarty at IIT Delhi focused on studies of complex biological systems, macromolecules, aqueous ionic solutions and network liquids using atomistic interaction potentials. Some of the important contributions that came out of these studies (Sastry 2001; Balasubramanian *et al*., 2002; Chanda and Bandyopadhyay 2005; Bandyopadhyay *et al*., 2005; Dastidar and Mukhopadhyay 2004; Bagchi and Biswas, 1999; Bagchi 2005; Senapati and

Chandra 2001; Mallik and Chandra 2006; Sharma R *et al*., 2006; Mudi *et al*., 2006) include (i) Solvation dynamics of water confined in micelles, (ii) Dynamics of hydrogen bonds in water and other associated liquids and their relations to vibrational spectral diffusion, (iii) Structure and dynamics of different kinds of interfacial systems such as liquid-solid, liquid-liquid, liquid-vapor and liquid-membrane interfaces, (iv) Dielectric behaviour of confined dipolar liquids, (v) Nature of supercritical systems, (vi) Behaviour of molecular solids under pressure, (vi) Conformational changes, interactions and solvation of proteins and DNA in water, (vii) Diffusion anomaly and entropy of network liquids, particularly water, liquid silica etc. Late nineties and beginning in early 2000s, the groups of R Biswas at S N Bose national Centre Kolkata, S Taraphder at IIT Kharagpur and S Senapati at IIT Madras also made important contributions on the structure, dynamics and reaction pathways in proteins, macromolecules, ionic liquids, binary systems and confined systems through combination of statistical mechanical theories and computer simulations (Biswas and Pal 2004; Kunor and Taraphder 2006; Chaitanya and Senapati 2008).

The early years of 2000s also saw the beginning of so-called first principles (or ab initio) simulations in India, largely facilitated by the emergence of parallel computers in the country. The groups of S Balasubramanian at JNCASR and Chandra at IIT Kanpur and a few others started working on first principles computer simulations usingquantum ab initio methods for energy and force calculations without involving any empirical potentials. Simulation studies at IIT Kanpur also focused on calculations of various nonlinear spectral properties such as those of transient hole burning vibrational spectroscopy, photon echo and two dimensional infrared (2D-IR) (Mallik *et al*., 2008; Ojha and Chandra, 2015). Studies were also made on proton transfer reactions in low dimensional systems and in enzymatic systems and also on electron localization in molecular clusters at finite temperatures (Bankura and Chandra, 2015). These latter studies made full use of the quantum many body potentials which allowed simulations of reactive events involving electronic rearrangement in the systems. The group of Balasubramanian also performed some of the early ab initio simulations of ionic liquids and unearthed several interesting interaction effects of the anions and cations in such systems (Payal and Balasubramanian 2014).

Over past 10 years, research groups working in areas of statistical mechanics and computer simulations have multiplied and spread to essentially all parts of the country. Now there are younger groups in IIT Guwahati, IACS Kolkata, IIT Bhubaneswar, IIT Hyderabad, IIT Delhi, IIT Kanpur, IIT Bombay, IISc Bangalore, NCL Pune, IISER Pune, IISER Kolkata, IISER Bhopal, IISER Trivandrum, NISER Bhubaneswar, many NITs, universities and other Institutes who are working in statistical mechanics and molecular simulations using classical, quantum or a combination of classical-quantum methods. See, for example, Refs. (Das and Paul, 2017; Chand *et al*., 2018; Dasari and Mallik, 2018; Kaur and Kashyap, 2018; Awasthi *et al*., 2016; Awasthi and Nair, 2017; Awasthi *et al*., 2018; Chugh and Ranganathan, 2016; Ghosh and Ranganathan, 2017; Chugh and Ranganathan, 2017; Sarkar *et al*., 2019; Maity and Reddy, 2018; Nandi *et al*., 2017; Hridya and Mukherjee, 2018; Sharma and Ghorai, 2018; Ahalawat and Murarka, 2017; Rout and Srinivasan, 2018; Shekar and Swathi, 2018; Kumawat and Chakrabarty, 2017; Palchowdhury and Bhargava, 2018; Mandal *et al*., 2018; Ahalawat and Mondal, 2018; Hasnain and Bandyopadhyay, 2015; Dutta and Nandi, 2015) for representative work from these groups in recent years. Also, many institutes now have multiple research groups working in statistical mechanics and computer simulations. For example, at IIT Kanpur, the groups of Ranganathan and Nair are involved, respectively, in studies of surface growth and rare events using advanced simulation methods of kinetic Monte Carlo and metadynamics (Awasthi *et al*., 2016; Awasthi and Nair, 2017; Awasthi *et al*., 2018; Chugh and Ranganathan, 2016; Ghosh and Ranganathan, 2017; Chugh and Ranganathan, 2017). These groups are also actively involved in methodological developments of computer simulations using advanced theoretical techniques and computer tools. It may be noted that the first three or four Theoretical Chemistry Symposium (TCS) hardly had any talks and lectures on statistical mechanics, with more than 90% devoted to quantum chemistry and scattering theory. However, by 2010, almost 40-50% of the lectures and posters contained some form of statistical mechanics. This is a clear indication of how the subject of statistical mechanics has grown as an active area of research among the practitioners of theoretical and

computational physical chemists in the country over past few decades.

Computer simulation studies of complex systems, both classical and quantum, are bound to grow in India because of a large number of young scientists present across India in various universities and institutes. The impact of such work shall depend on the originality of these young scientists in choosing the right problems to study. *In the eagerness of performing a publishable work, often the merit of selecting a good problem is forgotten*. We have seen such issues even in the international scene. While the area of computer simulations is in good shape, the area of analytical statistical mechanics is being less pursued. This is quite different in Physics Departments where more efforts are given in analytical work than numerical work. In future, statistical mechanics in India shall certainly venture into new areas.

A guiding principle of future research should be a close collaboration between theory and experiment. A major concern here is a lack of a vibrant experimental physical chemistry community in India. This lacuna can have a serious effect in future and needs to be mended on an urgent basis. Another important area where studies are lacking is at the interface of statistical mechanics and materials science.

Finally, we must emphasize that we do not claim to have made an exhaustive account of all the work that have been accomplished in India in the area of statistical mechanics and computer simulations. Our goal was to provide an impression, within a limited scope, of the kind of work that have taken place and what possibly could be future directions in this area. The references included in this article are only representative and they, by no means, capture the full breadth of work that have been published from India. The reader is directed to the homepages of various authors and also available literature in journals and monographs for more complete account of work published from various groups in the country.

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