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Computer Simulations of Ions, Dipoles, DNA Elasticity and Interfaces

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Final Report for Period: 01/2000 - 10/2004**Submitted on:** 12/21/2004**Principal Investigator:** Rasaiah, Jayendran C.**Award ID:** 9981336**Organization:** University of Maine**Title:**

Computer Simulations of Ions, Dipoles, DNA Elasticity and Interfaces

Project Participants**Senior Personnel****Name:** Rasaiah, Jayendran**Worked for more than 160 Hours:** Yes**Contribution to Project:****Post-doc****Name:** Noworyta, Jerzey**Worked for more than 160 Hours:** Yes**Contribution to Project:****Graduate Student****Name:** Koneshan, Siva**Worked for more than 160 Hours:** Yes**Contribution to Project:****Name:** Waghe, Aparna**Worked for more than 160 Hours:** Yes**Contribution to Project:****Name:** Vaitheeswaran, Subramanian**Worked for more than 160 Hours:** Yes**Contribution to Project:****Undergraduate Student****Name:** Fortune, Stephen**Worked for more than 160 Hours:** Yes**Contribution to Project:****Technician, Programmer****Other Participant****Research Experience for Undergraduates****Organizational Partners****Other Collaborators or Contacts**

Professor Ruth Lynden-Bell - The Queens University, Belfast U.K. and Cambridge University, Cambridge, U.K.

Dr. Liem. Dang -Pacific National Lab, Richland, Washington

Dr Gerhard Hummer - Chemical Physics Division, NIDDK, National Institutes of Health, Bethesda, MD

Activities and Findings

Research and Education Activities:

Findings: (See PDF version submitted by PI at the end of the report)

Training and Development:

The following students and postdoctoral fellows were trained with the resources provided by this grant:

- (a)Siva. Koneshan - graduate student (doctorate in Chemistry, completed)
- (b)Subramaniam . Vaitheeswaran - graduate student (doctorate in Physics, completed)
- (c)Jerzey. P. Noworyta (Ph.D Utah) - post doctoral fellow
- (d)Aparna Waghe - graduate student in Chemistry; Ph.D candidate
- (e)Hao Yin - graduate student in Chemistry, Ph. D candidate
- (f)Stephen. Fortune - undergraduate in biomedical engineering

Outreach Activities:

Journal Publications

J.P.Noworyta, S. Koneshan and J. C.Rasaiah., "Dynamics of Aqueous Solutions of Ions and Neutral Solutes at Infinite Dilution at Supercritical temperatures of 683K", J. Amer. Chem.Soc., p. 11194, vol. 122, (2000). Published

S. Koneshan and J.C.Rasaiah, "Simulation Studies of Aqueous Sodium Chloride at 298K and 683K.", J. Chem. Phys., p. 8125, vol. 113, (2000). Published

S. Koneshan, J. C. Rasaiah and L. X. Dang, "Computer Simulation Studies of Aqueous Solutions at Ambient and Supercritical Conditions using Effective Pair Potential and Polarizable Potential models of Water", J. Chem. Phys., p. 7544, vol. 114, (2001). Published

R. M. Lynden-Bell, J. C. Rasaiah and J. P. Noworyta, "Using Simulation to Study Solvation in Water", Pure. Appl. Chem., p. 1721, vol. 73, (2001). Published

J.C. Rasaiah and R. Lynden-Bell, "Computer Simulation Studies of the Structure of Ions and Nonpolar Solutes in Water", Philos. Trans. Roy. Soc A, p. 1545, vol. 359, (2001). Published

G. Hummer, J. C. Rasaiah and J. P. Noworyta, "Water Conduction through the Hydrophobic Channel of a Carbon Nanotube", Nature, p. 188, vol. 414, (2001). Published

A.Waghe, J. C. Rasaiah and G. Hummer, "Kinetics of Emptying and Filling of Carbon Nanotubes in Water", J. Chem. Phys., p. 10789, vol. 23, (2002). Published

S. Vaitheeswaran, J. C. Rasaiah and G. Hummer, "Electric Field and Temperature Effects on Water in the narrow Nonpolar Pores of Carbon Nanotubes", J.Chem. Phys., p. 7955, vol. 121, (2004). Published

S. Vaitheeswaran, H. Yin, J. C. Rasaiah and G. Hummer, "Water Clusters in Nonpolar Cavities", Proc. Nat. Acad. Sci., p. 17002, vol. 101, (2004). Published

S.Vaitheeswaran, H.Yin, J.C.Rasaiah, "Water between Plates in the presence of an Electric Field in an Open System", J. Phys. Chem. B., p. , vol. , (). Accepted

Books or Other One-time Publications

J. C. Rasaiah, "Statistical Mechanics of Strongly Interacting Systems", (2002). Book, Published
 Editor(s): Ed J. H. Moore and N. D. Spencer.
 Collection: Encyclopedia
 Bibliography: Encyclopedia of Chemical Physics and Physical Chemistry

Web/Internet Site

Other Specific Products

Contributions

Contributions within Discipline:

Ion transport in an aqueous medium is modulated by frictional forces: namely hydrodynamic and dielectric friction. This applies generally at ambient temperatures. Our work on ion and uncharged solute transport at supercritical temperatures has helped to elucidate the mechanism of transport in this region where solvent density fluctuations play an important part in controlling the rate of transport. We have also investigated the thermodynamic and structural properties of ionic solutions in the supercritical region where we identified the presence of solute clusters which move as an entity. This requires that the mobilities of positive and negative ions nearly the same when cluster formation occurs. The work on water penetration and intermittent pulsed conduction through the narrow pores of carbon nanotubes (CNT) published in Nature (2002) is our most important contribution to our discipline supported by this grant. The sensitivity of filling to small changes in the nanotube-water interactions through chemical modification suggests a water switch which can regulate the flow of water through the tube. It also suggests that water may even occupy hydrophobic cavities which we investigated and reported recently in PNAS (Dec 2004). Our work on CNT received wide publicity e.g C&E News (Nov 12, 2001 p.23) and other magazines which underscores its relevance and importance to our discipline. A commentary in Nature by Mark. Sanson and Phillip Begin (Nature 414, 156 2001) states that it that 'extends our understanding of how liquids behave on the nanoscale' and is 'directly relevant to the way in which evolution has fine-tuned different members of the aquaporin family in their relative permeability to water and glycerol'.

Contributions to Other Disciplines:

Our research involved the heavy use of simulation and the development of efficient methods to study water flow in carbon nanotubes. using parallel computers. We also developed new theoretical tools to study water occupancy in partially confined systems open to a reservoir, by calculating the grand partition function term by term using the chemical potential and density of the water reservoir as input parameters. This method was used in our research on the thermodynamics of filling carbon nanotubes and hydrophobic cavities.

Contributions to Human Resource Development:

The grant provided training for a postdoctoral fellow and students, at all levels. Graduate students S. Koneshan, S.Vaitheeswaran, A.Waghe, H. Yin and an undergraduate, Stephen Fortune, were members of the group at different times during the period of the grant. A post doctoral fellow, Dr. J. Piotr Noworyta, continued to work with the group with NSF support until he left in 2002 to take a position at the Warsaw Medical Institute in his home country Poland.

S. Koneshan received his Ph.D degree in Chemistry May 2000 under my direction and his thesis work led to six publications; four of them during the period of the current NSF grant.. He joined the Computer Science Department at Cornell University as a Postdoctoral Fellow to work with Professor Ron Elber on 'Ion Permeation in Gramicidin'. His work at Cornell received wide publicity on campus as well as in scientific community (Proteins 53, 63-80, 2003). He joined Johnson and Johnson as a scientist after completion of his work at Cornell. S.Vaitheeswaran received his Ph.D in Physics under my direction in May 2004 and is at The Institute of Physical Science and Technology at the University of Maryland where he is a Post doctoral fellow with Professor Dev. Thirumilai. Three papers resulted from his research (two published, one in press - see publication list); one paper appeared in Dec 2004 in the Proceedings of the National. Academy of Sciences .

Aparna Waghe is continuing her doctoral studies in Chemistry at the University of Maine and is expected to graduate in December 2005. She

has published one paper in the Journal of Chemical Physics and another based on her research is in preparation.

Hao Yin joined the group in 2002 as a doctoral student in Chemistry and is already coauthor of two papers on water in nonpolar cavities and water between plates in the presence of an electric field. He is expected to graduate in May 2006.

The theoretical and computational research of the PI's group continued to attract several visitors, notably Prof. Ruth Lynden Bell (Queens University, Belfast, U.K and Cambridge University, U.K.), Dr. Liem Dang (Pacific National Labs), Dr. Gerhard Hummer (N.I.H) and Professor Shekar Garde (Chemical Engineering Department, R.P.I). During their visits they gave talks at regular Departmental colloquia which contributed to the professional advancement of students and faculty.

Contributions to Resources for Research and Education:

A course on Computer Simulation Methods (CHY 573), inspired and motivated by our research continues to be taught by me in the department. Graduate students from Physics and Chemistry, took the course when it was taught last time. I also teach 'Statistical Thermodynamics' (CHY 673) to graduate students in Chemistry and Physics department (I have a joint appointment with Physics) and introduced students to molecular dynamics simulations. This was a direct spin off of our research interest and support of computational studies by the NSF.

Contributions Beyond Science and Engineering:

Categories for which nothing is reported:

Organizational Partners

Activities and Findings: Any Research and Education Activities

Activities and Findings: Any Outreach Activities

Any Web/Internet Site

Any Product

Contributions: To Any Beyond Science and Engineering

Activities and Findings

1. Research and educational activities.

The major research carried out during the period of this grant used computer simulation and theory to investigate (i) the transport of ions and nonpolar solutes in the water at ambient and supercritical conditions, (ii) water occupancy in confined systems such as carbon nanotubes and hydrophobic cavities and (iii) the behavior of water between plates in the presence of an electric field. Specifically the problems studied were:

- (a) Solvation thermodynamics, ion mobility and the diffusion of uncharged charged solutes in supercritical water.(with R. Lynden-Bell, S. Koneshan, J. P. Noworyta, L. Dang).
- (b) Water conduction through hydrophobic channels of carbon nanotubes. (with J. P. Noworyta and G. Hummer) and the kinetics of filling and emptying carbon nanotubes in water. (with A.Waghe and G. Hummer)
- (c) Electric field effects and temperature coefficients of water occupancy of carbon nanotubes with water (with S.Vaitheeswaran and G. Hummer)
- (e) The structure and stability of water clusters in nonpolar hydrophobic cavities (with S.Vaitheeswaran, H.Yin and G. Hummer)
- (f) The behavior of water between plates in the presence of an electric field in an open system (with S.Vaitheeswaran and H.Yin)

Four graduate students (S. Koneshan, A.Waghe, S.Vaitheeswaran and H. Yin), an undergraduate (S. Fortune) and a postdoctoral fellow (Dr. J .P. Noworyta) received training under this project. Three of them (S. Koneshan, A.Waghe and S.Vaitheeswaran) were supported at various times by the grant.

We also collaborated with Professor Ruth Lynden-Bell of Queens University Belfast U.K, Dr. Liem Dang of the Pacific National Labs, WA and Dr. Gerhard Hummer of the National Institutes of Health MD on several of the projects listed above. These collaborations have lead to an xchange of ideas and visits by students and/or the PI (listed in parenthesis) to The Pacific National Labs (S. Koneshan) and the National Institutes of health (S. Vaitheeswaran and J. C. Rasaiah). Professor Ruth Lynden-Bell visited the University of Maine in connection with collaborative research.

2. Major findings resulting from these activities.

(a) Solute Transport and Ion Mobility in Supercritical water. Ion and uncharged solute transport play an important role in solution chemistry at ambient conditions and even in the supercritical region. Our previous research was directed towards understanding the characteristic trends shown by ion mobilities at infinite dilution in aqueous solutions at room temperature (25°C), and the relative importance of hydrodynamic and dielectric contributions to the friction coefficient of an ion. In the current work, supported by the NSF grant, we studied ion mobility and the thermodynamics of solvation at supercritical temperatures.

Dr. J.P. Noworyta, a postdoctoral fellow, S. Koneshan and the PI carried out molecular dynamics simulations of ions and uncharged solutes in water at a supercritical temperature of 683K and a solvent density of 0.335gcm^{-3} , using the extended simple point charge model (SPC/E model) for water and related solute-water potentials. They compared the structure and dynamics of ions and nonpolar solutes in these solutions with the earlier work done in our group at ambient temperatures (298K and solvent density of 0.997gcm^{-3}). The distinct maxima in the ion mobility of cations and anions as a function of size that occurs at ambient temperatures is absent in the supercritical solution at low density, but returns when the density is increased to 0.997g cm^{-3} . This shows that the density of the solvent, rather than the temperature, plays an important role in determining whether a maximum occurs. The presence of separate maxima for cations and anions is related to the charge asymmetry of the water molecule. We also showed that the mechanism of diffusion of ions and uncharged solute molecules in the low density supercritical region is also controlled by solvent density fluctuations besides the hydrodynamic and dielectric friction effects that dominate their behavior at ambient temperatures. This provided a theoretical explanation of the ratio of the diffusion coefficients of charged and uncharged solutes of the same size in the low density supercritical region.

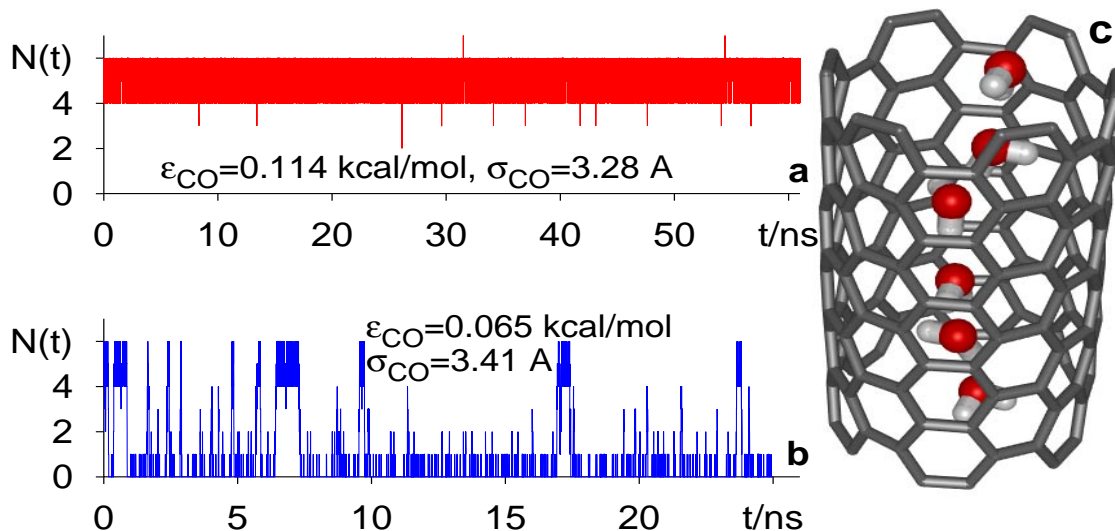
S. Koneshan together with Dr. Liem Dang and the PI studied the diffusion coefficients of and structure of infinitely dilute aqueous ionic solutions at ambient and supercritical conditions using different models for water; the extended simple point charge (SPC/E) model and the renormalized polarizability (RPOL) model. The polarizability is treated explicitly in the RPOL model and approximately in the SPC/E model which is parameterized at ambient temperatures. Surprisingly, the electronic polarizability had only a small effect on the structure and dynamics of infinitely dilute ions at the solvent densities considered in the study. This paper has led to further studies by the group at Texas (Rossky) to unravel the reasons for this unusual behavior.

Koneshan and the PI also studied 1M and 0.5 M aqueous solutions of sodium chloride at ambient and supercritical temperatures using both discrete and simple point charge models for water. The solvent densities were 0.997gcm^{-3} at 298K and 0.35gcm^{-3} at 683K. The studies reveal the presence of significant ion clustering that goes beyond simple ion pairing in supercritical solutions. Positive and negative ions were observed to move together as entity over a period of at least 200ps making their mobilities the same under these conditions.

Our work on the thermodynamics, structure and dynamics of ions and uncharged solutes at ambient and supercritical temperatures was investigated and published and summarized separately in a review article written by the PI and Lynden-Bell (Philos. Trans. Roy. Soc. 2002).

(b) Water conduction through hydrophobic channels of carbon nanotubes. (with J. P. Noworyta, and G. Hummer). A very novel and exciting new phase of our research began with the study of water occupancy and conduction through hydrophobic channels of carbon nanotubes (CNT) in collaboration with Dr. Gerhard Hummer at the National Institutes of Health (Nature, 2001) and Dr. J. P. Noworyta, a postdoctoral fellow at Maine supported by the NSF grant. Previously the PI and R. Lynden-Bell had studied ion

mobility in aqueous solutions confined to cylindrical channels with periodic boundary conditions to replicate the channel along its axis. The channel was not open to a reservoir. It came as a surprise to learn that a carbon nanotube of finite length and width of about 8Å open to a reservoir would rapidly fill up with water despite the hydrophobic nature of the channel wall. Small changes in the nanotube-water interactions, corresponding to chemical modification may lead to emptying. The figure shows the filling/or emptying of the channel with $N(t)$ water molecules as a function of time t for two slightly different nanotube-water interaction parameters.



The Free energy of occupancy fluctuations $F(N) = -\ln P(N)$ was determined from the probability $P(N)$ of finding N water molecules in the channel. Chains of hydrogen-bonded water molecules in single file moved through the tube in short pulse like bursts at intervals of about one nanosecond. The kinetics of emptying and filling was studied with Aparna Waghe, a chemistry predoctoral student at Maine, and the transition state was determined to be the filled tube less one water molecule required to complete the hydrogen bonded chain with the external reservoir. A physics graduate student, S.Vaitheeswaran joined the PI and Hummer to investigate the interaction of electric fields along the tube axis with water chains in CNT. By evaluating the grand partition function term by term, we showed that electric fields favor filling nanotubes tuned to be empty. The entropy and energy contributions to the free energy of filling were determined from the temperature dependence of the occupancy probabilities. The energy, but not the entropy, was found to be sensitive to the nanotube-water interactions. The entropy of filling is positive and favors filling for all occupancy numbers except the completely filled state when it is negative. The minimum in the free energy of the filled state is thus driven by the favorable energy due to the van der waals dispersion forces that prevail between water and carbon atoms even in the hydrophobic environment of the CNT.

(c) **Water clusters in nonpolar hydrophobic cavities.** The discovery that water can occupy hydrophobic channels of carbon nanotubes suggests that it may also occupy hydrophobic cavities similar to those found in the interior of proteins. The PI and

Hummer investigated this with S. Vaitheeswaran and a Hao Yin, a graduate student in Chemistry who had joined our group. We found that small hydrophobic cavities and even fullerenes (C_{140} and C_{180}) can be filled by water molecules which form clusters similar to those studied spectroscopically in the gas phase (e.g. Saykally at Berkeley). Water filling is sensitive to the size of the cavity and to the strength of the cavity water interactions. The water clusters are hydrogen bonded but unlike the single file water chain found in CNT. Beginning with the trimer, the clusters evolve as cyclic structures through to the pentamer with each water molecule donating a hydrogen bond to a nearest neighbor and accepting another H-bond from another. As in the gas phase clusters, the hexamer signals a cross-over from cyclic to cage-like structures of coexisting isomers as more water molecules are added to form an octamer with has the oxygen atoms of water molecules at the vertices of a cube. Calculations of the configurational specific heats of an encapsulated water cluster as a function of temperature showed a maximum, indicating a "melting" transition to disordered states with broken hydrogen bonds. Our studies published in PNAS (Dec 7 2004) invite the possibility that folded proteins may contain water molecules in interior cavities.

(d) Water between hydrophobic plates in the presence of an electric field in an open System (with S.Vaitheeswaran, H.Yin and J.C. Rasaiah)

Molecular dynamics simulations of water at 298 K and 1 atm pressure were used to investigate the electric field dependence of the density and polarization density of water between two graphite-like plates of different sizes ($9.8 \times 9.2 \text{ \AA}$ and $17.7 \times 17.2 \text{ \AA}$) in open systems for plate separations of 8.0, 9.5 and 16.4 \AA respectively. The interactions with water were tuned to "hard wall-like" and "normal" carbon-oxygen hydrophobic potentials. Water between the larger plates at 16.4 \AA separation was layered, but metastable with respect to capillary evaporation at zero field. Applying a field decreased the density of the water between plates, in apparent contradiction to thermodynamic and integral equation theories of bulk fluid electrostriction that ignore surface effects. Water, between "hard wall-like" plates at narrower separations of 9.5 \AA and less, showed spontaneous but incomplete evaporation at zero field during the time scale of simulation. Evaporation was further enhanced by an electric field. No such evaporation occurred for the smaller plates with the "hard wall-like" potential at a separation of 8.0 \AA at zero field, signaling a crossover in behavior as the plate dimension decreases. The density of water between plates still decreases with the applied field. These observations have implications for the behavior of narrow water films between hydrophobic surfaces in physical and biological systems.