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Special Issue on Theoretical Chemistry/Chemical Dynamics

Guest Editors: BIMAN BAGCHI · DAVID CLARY · N SATHYAMURTHY

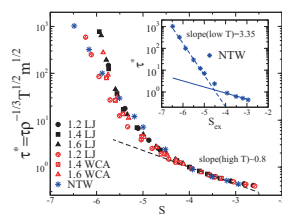
Regular Articles

Preface

Biman Bagchi, David Clary and N Sathyamurthy791–792

Validity of the Rosenfeld relationship: A comparative study of the network forming NTW model and other simple liquids

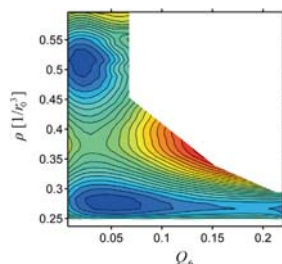
Atreyee Banerjee, Manoj Kumar Nandi and Sarika Maitra Bhattacharyya793–800



Simulated results for a model network forming liquid (NTW) are compared with other simple liquids. The plot shows at high temperatures all the systems follow the Rosenfeld relation with an universal exponent. However, only the NTW model shows a validity of the scaling law at low temperatures which is similar to that found for ionic melts.

A free energy study of the liquid-liquid phase transition of the Jagla two-scale potential

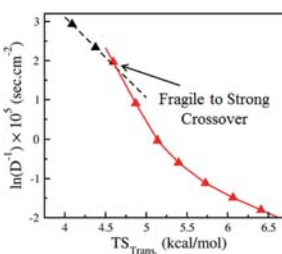
Francesco Ricci and Pablo G Debenedetti801–823



Rigorous free energy calculations are performed to demonstrate the existence of a liquid-liquid phase transition (LLPT) in the spherically-symmetry two-scale Jagla potential. We also calculate the surface tension associated with the LLPT and investigate the relaxation times of density and bond-orientational order to gain further insight into the LLPT phenomenon.

Connecting diffusion and entropy of bulk water at the single particle level

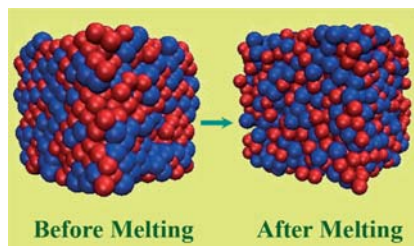
Debasis Saha and Arnab Mukherjee825–832



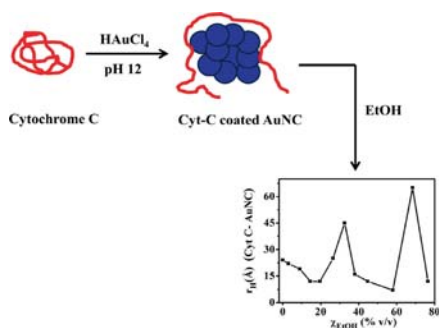
Translational and rotational entropy of individual water molecules have been calculated at different temperatures. The thermodynamic fragility in terms of translational entropy has been measured. The thermodynamics have been connected with the dynamics by correlating the diffusion coefficient with translational entropy at different temperatures by using analog of Adam-Gibbs relation.

Breakdown of universal Lindemann criterion in the melting of Lennard-Jones polydisperse solids

Sarmistha Sarkar, Chandramohan Jana and Biman Bagchi . . .833–840



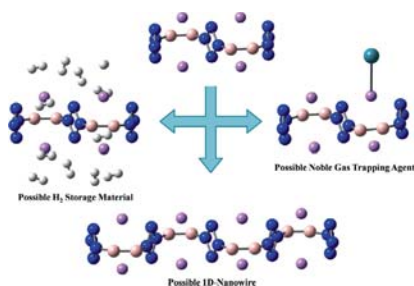
Lindemann ratio (scaled root mean square displacement) is found to be strongly dependent on size of particles - smaller particles have higher values than bigger ones near melting transition of LJ polydisperse solid. Underlying cause of breakdown of universal Lindemann criterion is related to greater tendency of partial segregation of smaller particles prior to melting.



Size and Structure of Cytochrome-c bound to Gold nano-clusters: Effect of Ethanol

Catherine Ghosh, M D Asif Amin, Biman Jana and Kankan Bhattacharyya841–847

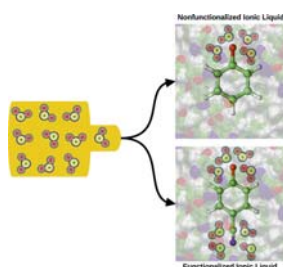
Size, conformation dynamics and structure of cytochrome c (Cyt C) bound to gold nanoclusters (AuNC) have been studied using fluorescence correlation spectroscopy (FCS) and circular dichroism (CD). The CD spectra of Cyt C indicate that the helical structure is almost completely lost on binding to AuNC signifying unfolding. Addition of ethanol causes partial restoration of structure of Cyt C. FCS data indicate that both the size and conformational relaxation time of Cyt C bound to AuNC vary non-monotonically with an increase in ethanol content.



Modeling of 1-D Nanowires and analyzing their Hydrogen and Noble Gas Binding Ability

Sudip Pan, Ranajit Saha, Ashutosh Gupta and Pratim K Chattaraj.849–858

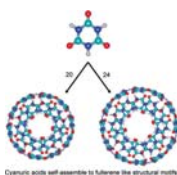
The B-B bonds in $[\text{N}_4\text{-B}_2\text{-N}_4]^{2-}$, $[\text{N}_4\text{-B}_2\text{-N}_4\text{-B}_2\text{-N}_4]^{4-}$ and $[\text{N}_4\text{-B}_2\text{-N}_4\text{-B}_2\text{-N}_4\text{-B}_2\text{-N}_4]^{6-}$ possess some degree of triple bond character. These anionic systems can be stabilized by combining with an adequate number of M^+ ($\text{M} = \text{Li}, \text{Na}, \text{K}$) ions. It opens up the possibility of designing a long 1-D nanowire. The Li centers of this nanowire can bind hydrogen molecules and noble gas atoms effectively.



Molecular Dynamics Investigation of Efficient SO_2 Absorption by Anion-Functionalized Ionic Liquids

Anirban Mondal and Sundaram Balasubramanian859–872

Efficient absorption of SO_2 by anion-functionalized ionic liquids has been studied using quantum mechanical and molecular dynamics simulation methods. Improved absorption capacity at much lower desorption cost has been found to be the consequence of SO_2 -cation interaction via dispersion forces and multiple-site interactions of SO_2 with anions.



Nanoclusters of Cyanuric Acid

M Elango, V Subramanian and N Sathyamurthy.873–881

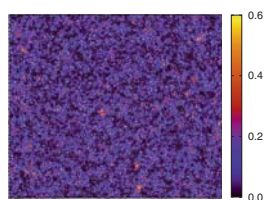
This article demonstrates that clusters of cyanuric acid with complementary hydrogen bonding interaction sites could result in the formation of bowls and balls in addition to the well-known planar sheet structures.



A model with charges and polarizability for CS_2 in an ionic liquid

Ruth M Lynden-Bell and Anthony J Stone883–890

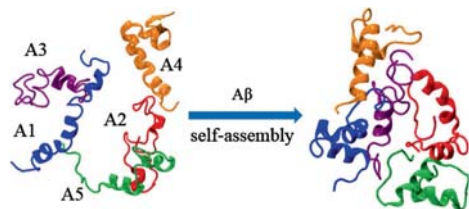
The picture shows the following: left: *ab initio* electrostatic potential (voltage) on the $\text{vdW} \times 1.5$ surface of CS_2 ; middle: difference between 3-site model and *ab initio*; right: difference between 7-site model and *ab initio*.



Excess vibrational modes of a crystal in an external non-affine field

Saswati Ganguly and Surajit Sengupta891–897

We show that it is possible to enhance non-affine displacement fluctuations in a crystal using an external field. Although transient, these fluctuations can shift the phonon density of states to low frequencies and cause “Boson peak” like phenomenon in an otherwise perfect crystal without quenched disorder.



In silico studies of the early stages of aggregation of $A\beta_{42}$ peptides

Prabir Khatua and Sanjoy Bandyopadhyay 899–909

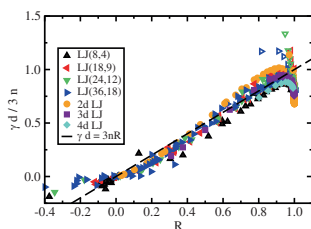
Molecular dynamics simulations were performed to probe the early stages of aggregation of $A\beta_{42}$ peptides. The calculations revealed that the helix–helix linkage plays an important role in bringing the unstructured regions of the monomers closer for self-assembly. Further, the nucleated oligomer was found to be stabilized primarily by nonpolar inter-peptide interactions.



Stabilisation of the [6]-prismane structure by silicon substitution

Asif Equbal, Shwetha Srinivasan
and Narayanasami Sathyamurthy. 911–917

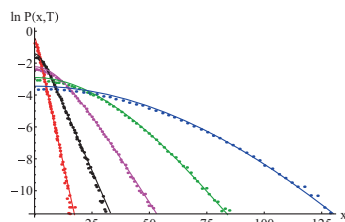
Ab initio calculations show that the stability of the [6]-prismane structure increases with an increase in the substitution of carbon atoms in the individual benzene rings by silicon or germanium atoms.



Density-scaling exponents and virial potential-energy correlation coefficients for the $(2n, n)$ Lennard-Jones system

Ida M Friisberg, Lorenzo Costigliola and Jeppe C Dyre 919–928

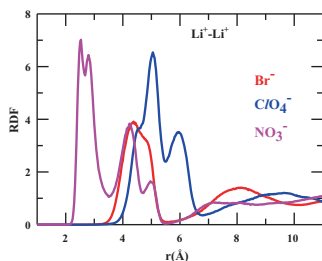
The paper presents numerical data for the density-scaling exponent γ and the virial potential-energy correlation coefficient R for generalized $(2n, n)$ Lennard-Jones (LJ) systems. An unanticipated linear relation is observed between R and a properly scaled version of γ .



Diffusing diffusivity: a new derivation and comparison with simulations

Rohit Jain and K L Sebastian. 929–937

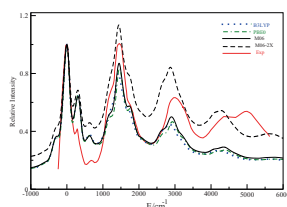
A model of diffusing diffusivity is analyzed and exact analytical results are obtained. The MSD is shown to vary linearly with time at all times yet the pdf is not Gaussian at all times. A comparison of these results is also made with the numerical results of Chubynsky and Slater.



Microstructures and their lifetimes in acetamide/electrolyte deep eutectics: anion dependence

Suman Das, Biswaroop Mukherjee and Ranjit Biswas 939–951

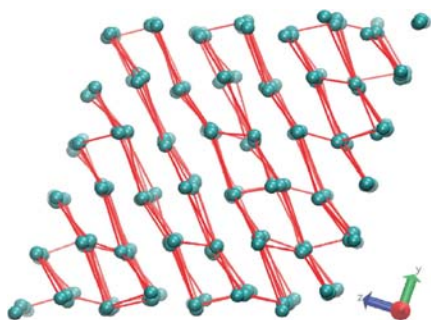
Molecular dynamic simulations have been carried out with three Acetamide/Electrolyte deep eutectics with an aim to characterize various microscopic structures and their lifetimes. We have analysed how the shape and size of anions dictate the interactions among molecules resulting in complexes of varying size and lifetime.



A comparative study of the performance of some density functionals for vibronic spectra

Ch Sridhar Reddy and M Durga Prasad. 953–961

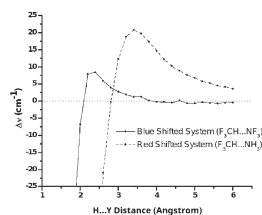
Computed vibronic spectra of four molecules, tetracene, octatetraene, anthracene and pyrene are compared to the experimental spectra with a view to determine the functional that can give the best description.



A molecular dynamics calculation of solid phase of malonic acid: role of hydrogen-bond chains and the elastic constants

Sathya S R R Perumal and Yashonath Subramanian. 963–974

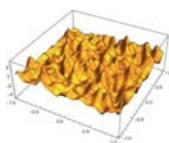
The calculation reports the lifetime and activation energies of hydrogen bond chains and demonstrates that there is a relation between direction of the hydrogen bond chains and elastic constants along that direction. Presence of hydrogen bonds along a given crystallographic direction leads to larger elastic constants. The picture shows a view down the **a** direction. Cyan dots represent centre of mass of malonic acid molecules in the triclinic crystal phase and red lines indicate hydrogen bonds between them. Note the existence of hydrogen bond chains along [011] direction.



A computational investigation of the red and blue shifts in hydrogen bonded systems

Mitradip Das and Swapan K Ghosh. 975–981

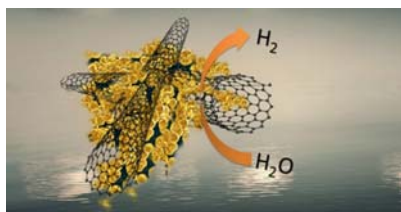
The blue and red shifts in vibrational frequency in X—H...Y hydrogen bonded systems as a function of H—Y distance are shown to correlate well with the atomic charges on H and Y as well as other electrostatic parameters.



Trajectories of Brownian particles with space-correlated noise

Edoardo Milotti 983–988

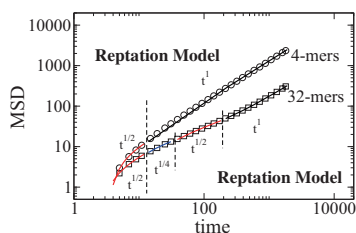
Spatially correlated, fluctuating random fields that drive Brownian particles produce some unexpected effects when the particles are close to one another.



Facile charge transport in FeN_x/Mo₂N/CNT nanocomposites for efficient hydrogen evolution reactions

Kasinath Ojha, Shivali Banerjee and Ashok K Ganguli 989–997

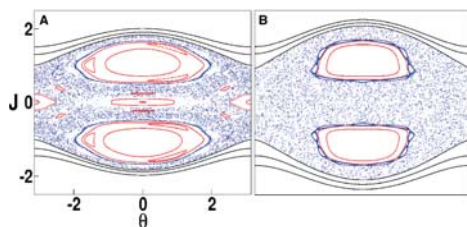
Introducing iron nitride in composite with molybdenum nitride leads to higher HER activity in acidic media. The *in situ* growth of CNTs in the composites enhances the conductivity and decreases the charge transfer resistance.



A coarse-grained model based on core-softened potentials for anomalous polymers

Ronaldo J C Batista, Evy A Salcedo Torres, Alan Barros de Oliveira and Marcia C B Barbosa 999–1003

Density and diffusion anomalies are present in the core-softened polymeric systems. The mobility of the macromolecules is Rouse-like for the small polymers and Entangle-like for the large polymers.



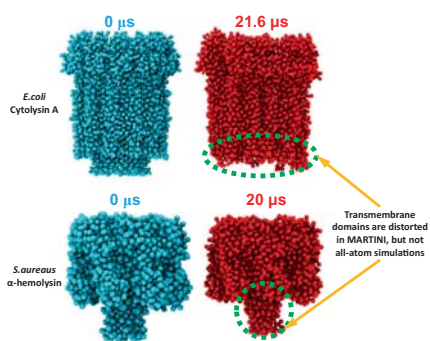
Controlling the quantum rotational dynamics of a driven planar rotor by rebuilding barriers in the classical phase space

Archana Shukla and Srihari Keshavamurthy. 1005–1016

This work aims to control the rotational excitations of an ac-driven planar rotor, a model for rigid diatomic molecules, by rebuilding barriers in the classical phase space. Our studies are relevant to understanding the role of the chaotic regions in dynamical tunneling and for molecular alignment using bichromatic fields.

Comparison of coarse-grained (MARTINI) and atomistic molecular dynamics simulations of α and β toxin nanopores in lipid membranes

Rajat Desikan, Swarna M Patra, Kumar Sarthak,
Prabal K Maiti and K G Ayappa 1017–1030



Multimeric and non-selective transmembrane pores formed by bacterial toxins on the host cell cause cell death, and hence elucidating membrane-protein interactions accurately in molecular models is important for unraveling biological phenomena at molecular resolution. A comparison of coarse-grained (MARTINI) and all-atom simulations for two prototypical pores in lipid membranes show that the transmembrane domains of both pores undergo significant distortions in MARTINI but not in all-atom simulations. Additionally, transmembrane proteo-lipid arcs show large shape distortions with a tendency to close in the MARTINI simulations. This indicates that both inter-protein and membrane-protein interactions in the MARTINI framework must be refined further.

Unfolding intermediates of the mutant His-107-Tyr of human carbonic anhydrase II

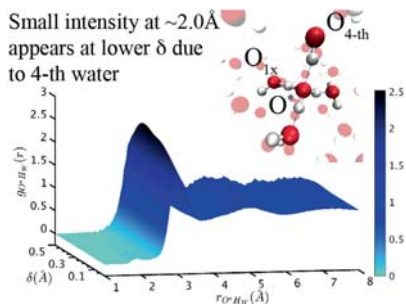
Srabani Taraphder, Puspita Halder, Tanmoy Kumar Paul and
Satyajit Khatua. 1031–1044



We present a novel computational methodology of extracting representative structures of putative unfolding intermediates of a large protein from high temperature classical MD simulations. The extracted structures are investigated to assess their aggregation propensity and projected catalytic activity.

Role of solvation structure in the shuttling of the hydrated excess proton

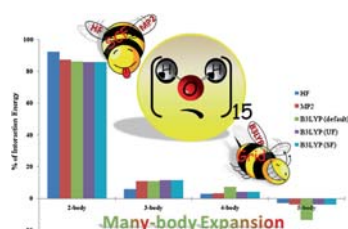
Rajib Biswas and Gregory A Voth 1045–1051



Hydrated excess proton transfer events in liquid water are highly coupled with local solvent orientations than previously thought. The weak hydrogen bond accepting nature of the hydronium helps to create water-like solvation environment around hydronium. This pre-solvated configuration facilitates the proton transfer process in liquid water. Proton sharing parameter-dependent radial distribution function shows the tiny intensity at 2.0 Å, which arises from the 4th water molecule solvating the hydronium moiety.

On the origin of spurious errors in many-body expansion for water cluster

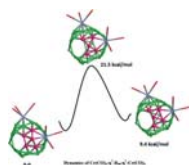
Soumen Saha, M Ram Vivek and G Narahari Sastry 1053–1060



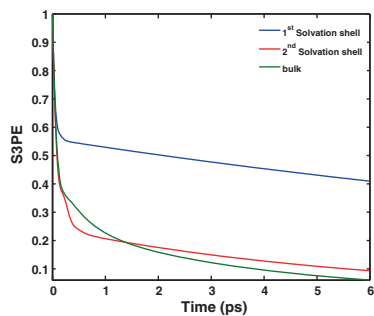
This study makes an attempt to investigate the effect of convergence criteria on two- to five-body energy terms and their contributions to the interaction energy of $(\text{H}_2\text{O})_{15}$ cluster. The erroneous results of many-body terms originated from cheaper convergence thresholds set as default criteria.

The dynamic behavior of the exohedral transition metal complexes of B_{40} : η^6 - and η^7 - $\text{B}_{40}\text{Cr}(\text{CO})_3$ and $\text{Cr}(\text{CO})_3$ - η^7 - B_{40} - η^7 - $\text{Cr}(\text{CO})_3$

Naiwrit Karmodak and Eluvathingal D Jemmis 1061–1067



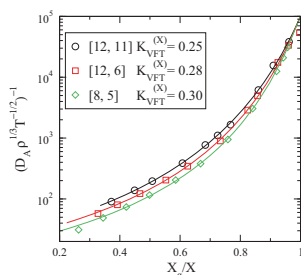
The exohedral complexation of the seven membered rings of B_{40} with $\text{Cr}(\text{CO})_3$ increases the barrier height for interconversion of six to seven membered rings.



Vibrational echo spectral observables and frequency fluctuations of hydration shell water around a fluoride ion from first principles simulations

Deepak Ojha and Amalendu Chandra 1069–1080

Solvation shell dynamics of water molecules in different solvation shells of fluoride ion is studied using vibrational echo spectral observables from first principles simulations. The decay of FTCF, S3PE and SNL for water molecules in first solvation shell show multiple timescales which can be associated with ion-water hydrogen bond lifetime and residence time of water in the solvation shell.



Density dependence of relaxation dynamics in glass formers, and the dependence of their fragility on the softness of inter-particle interactions

Anshul D S Parmar, Pallabi Kundu and Srikanth Sastry . . . 1081–1091

We analyse fragility, which quantifies the rapidity of variation of relaxation times, using density as the control variable, for model glass formers with varying softness of interactions. Using scaled variables, we find – and rationalise thermodynamically by computing configurational entropy – that fragility increases with softness, contrary to previous work.