1. Density anomaly in a waterlike model confined between plates

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Water exhibits thermodynamic, dynamic and structural anomalous properties when compared with other substances. While most liquids contract upon cooling, water expands below T = 4ºC at ambient pressure, which characterize the density anomaly. Recently, confined water has been receiving a lot of attention due the its applications in industrial and biological systems. In this work, we explore the effects of confinement in the pressure-temperature phase diagram of liquid water confined between plates. We employ molecular dynamic simulations in the NVT ensemble to study the systems. Water is modeled by a two length scale effective potential in which the particle-particle interaction has a repulsive shoulder at $r/\sigma_p \approx 1$ *and a very small attractive part around* $r\sigma_p \approx 3.8$. *In z direction, the particles are confined between two flat, rough and neutral plates, and the particle-plate interaction is given by a Weeks-Chandler-Andersen potential (WCA). We found that this system exhibits layering density in z direction and that the number of layers depends on the distance* d/σ_p *between the plates. The pressure-temperature phase diagram of the confined system shows the presence of density, diffusion and structural anomalous behavior similar to the behavior observed in bulk water, but for lower temperatures and higher densities.*

2. Effective dielectric constant of confined water in nanoestructured carbon nanotube electrodes

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At the electrode-solution region of an electrolytic cell, a double layer capacitance comes out as consequence of the confined fluid within the atomic layer of ions formed close the solid-liquid interface. For a plain, smooth surface, this capacitance is consistent with ordinary water confined to a layer of nanometric dimensions. We made a set of structured carbon nanotube (NTC) electrodes and performed cyclic voltammetry measurements. Some electrodes were also functionalized with platinum nanoparticles. Double layer capacitance values were obtained as function of the maximum applied voltage in the cycle and its voltage rate. Your results indicate that ionic confinement close the complex geometry of the structured electrodes may lead to water dielectric constant in the double layer that differs from its bulk values.

3. Efficient Monte Carlo simulation of fluid systems at low temperatures

Alexandra Valentim and Carlos E. Fiore

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We perform Monte Carlo simulation of fluid systems at the phase transition regimes. In particular, we consider the Blume-Capel, Blume-Emery-Griffiths and Bell-Lavis liquid water models. A common feature is that at low temperatures, all of them present strong first-order transitions, a regime difficult to simulate by means of standard algorithms because the free-energy minima are separate by large barriers. Consequently standard one flip algorithms do not guarantee an ergodic simulation. In order to circumvent these difficulties, we consider the simulated tempering (ST), that consists of making the temperature as a dynamical variable: it assumes distinct values from a set { T1 < T2 < … < Tn }. The central idea is that evolution at higher T's strongly facilitates the crossing the free-energy barriers, then allowing uniform visits to the multiples regions of a fragmented phase-space. The first aim of this study consists of analyzing the role of the temperature schedule of the ST. We consider different criteria for distributing the temperatures, such as arithmetic, geometric, arithmetic progression in inverse temperature and the constant entropy method (CEM). The CEM uses the constant increase of entropy as a criterion to choose the temperature schedule. The analysis of the convergence toward the stationary from a non-typical configuration and the frequency of tunneling between phases shows that the distribution of temperatures play an important role in the visit of the phase space and the CEM criteria seems to be superior than the others, in agreement with a previous study through Parallel Tempering.

4. Thermodynamics of trajectories of the 1D-Ising model

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We present a numerical study of the one-dimensional Ising model with Glauber dynamics where we apply the large deviations formalism [1] to study the properties of ensembles of trajectories. We confirm the dynamical ferromagnetic transition which has been theoretically predicted recently at zero magnetic field [2]. The transition can be understood with finite size scaling theory taking the observational time as the size of the system. In this way we have measured the exponents of the transition which are compared with those belonging to the 2D-Ising universality class. Also, we have extended the phase diagram of [2] by considering the case of a non-zero external magnetic field. We discuss general implications of our results for the relation between thermodynamic and dynamic phase structure.

[1] J. P. Garrahan, R. L. Jack, V. Lecomte, E. Pitard, K. van Duijvendijk, and F. van Wijland, Phys. Rev. Lett. 98, 195702 (2007).

[2] Robert L Jack and Peter Sollich, Prog. Theor. Phys. Supp. 184, 304 (2010)

5. Liquid crystal phase and water-like anomalies in a core-softened shoulder-dumbbells system

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Using molecular dynamics we investigate the thermodynamics, dynamics and structure of 250 diatomic molecules interacting by a core-softened potential. This system exhibits thermodynamic, dynamic and structural anomalies: a maximum in density-temperature plane at constant pressure and maximum and minimum points in the diffusivity and translational order parameter against density at constant temperature. Starting with very dense systems and decreasing density the mobility at low temperatures first increases, reaches a maximum, then decreases, reaches a minimum and finally increases. In the pressure-temperature phase diagram the line of maximum translational order parameter is located outside the line of diffusivity extrema that is enclosing the temperature of maximum density line. We compare our results with the monomeric system showing that the anisotropy due to the dumbbell leads to a much larger solid phase and to the appearance of a liquid crystal phase.

6. Dynamic properties of water confined with hydrophobic plane walls

Gaston Ferrara

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Near a hydrophobic wall, the structure as well as dynamics of water molecules change as compared to bulk water. The scope of the perturbation introduced by the presence of hydrophobic wall has been subjecy of some controversy in recent publications. To study this problem we simulate a system of water confined by two parallel hydrophobic amorphous walls by Molecular Dynamics. The hydrophobic wall was built using a binary mixture of Lennard-Jones particles, defining the parameters of interaction of this mixture so that the diffusion coefficient of the mixture is much less than that corresponding to the water in the temperature range chosen (near ambient temperautre). For water we used the SPC/e model. We studied the hydrogen-bond network, density and density time correlations as a function of the distance from the wall at five reference temperatures: 270K, 285K, 300K, 315K and 330K. The results show both for structural analysis or dynamics that the presence of the wall produced one perturbation of several orders of magnitude higher than what was believed in recent decades, showing one strong coincidence with some recent experimental results.

7. Dynamical and structural heterogeneities near liquid-liquid phase transitions: The case of gallium

Samuel Cajahuaringa, Maurice de Koning and Alex Antonelli

Universidade Estadual de Campinas, Brazil

Recently, it was found through molecular dynamics simulations that liquid elemental gallium, described by a modified embedded-atom model, exhibits a liquid-liquid phase transition (LLPT) in the supercooled regime, between a high-density liquid (HDL) and a low-density liquid (LDL), about 60 K below the melting temperature [D. A. C. Jara, et al., J. Chem. Phys. 130, 221101 (2009)]. In this work, we studied the dynamics of supercooled liquid gallium near the LLPT. Our results show a large increase in the plateau of the self-intermediate scattering function (beta-relaxation process) and in the non-Gaussian parameter, indicating a pronounced dynamical heterogeneity upon the onset of the LLPT. The dynamical heterogeneity of the LDL is closely correlated to the structural one, since the fast diffusing atoms belong to high-density domains of predominantly 9-fold coordinated atoms, whereas the slow diffusing ones are mostly in low-density domains of 8-fold coordinated atoms. The energetics suggests that the reason for the sluggish dynamics of LDL is due to its larger cohesive energy as compared to that of the HDL. Work in collaboration with Samuel Cajahuaringa and Maurice de Koning. Published in J. Chem. Phys. 136, 064513 (2012). Work supported by Fapesp, CNPq, Capes, and Faepex/Unicamp.

8. Water in TiO_2 Nanopores: a study on structure, dynamics, phase behavior and optical properties of confined water

Estefanía Gonzalez Solveyra, Verónica Sánchez, Ezequiel de la Llave, Valeria Molinero, Galo Soler-Illia and Damian A. Scherlis

Universidad de Buenos Aires, Argentina

Molecular dynamics simulations of water confined in TiO_2-rutile pores of diameters 1.3, 2.8 and 5.1 nm, were carried out at various water contents. Water density and diffusion coefficients were obtained as a function of the distance from the surface. The proximity to the interface affects density and diffusivity within a distance of around 10 Å from the walls, beyond which all properties tend to converge. Different filling mechanisms were observed as a function of the pore size. Capillary condensation takes place in equilibrium for the 2.8 and 5.1 nm pore. In the former case, the surface density increases uniformly with filling until condensation, whereas in the larger nanotube, a cluster of water molecules develops on a localized spot on the surface for fillings just below transition. In the smaller pore, no phase transition is detected. For all the systems studied, the first monolayer of water is strongly immobilized on the interface, thus reducing the accessible or effective diameter of the pore by around 0.6 nm. Finally, our results show how confinement affects the dynamic properties of water inside the pores. The mobility observed for the water molecules is strongly dependent on their proximity to the surface as well as the rotational dynamics, having in turn a significant impact on the dielectric and optical responses of the confined water.

9. Aqueous electrolytes confined within functionalized silica nanopores

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Molecular dynamics simulations have been carried out to investigate structural and dynamical characteristics of NaCl aqueous solutions confined within silica nanopores in contact with a "bulk-like" reservoir. Two types of pores, with diameters intermediate between 20 Å and 37.5 Å, were investigated: The first one corresponded to hydrophobic cavities, in which the prevailing wall-solution interactions were of the Lennard-Jones type. In addition, we also examined the behavior of solutions trapped within hydrophilic cavities, in which a set of unsaturated O-sites at the wall were transformed in polar silanol Si–OH groups. In all cases, the overall concentrations of the trapped electrolytes exhibited important reductions that, in the case of the narrowest pores, attained 50% of the bulk value. Local concentrations within the pores also showed important fluctuations. In hydrophobic cavities, the close vicinity of the pore wall was coated exclusively by the solvent, whereas in hydrophilic pores, selective adsorption of Na+ ions was also observed. Mass and charge transport were also investigated. Individual diffusion coefficients did not present large modifications from what is perceived in the bulk; contrasting, the electrical conductivity exhibited important reductions. The qualitative differences are rationalized in terms of simple geometrical considerations.

10. Anomalous water-like properties in a lattice model that has only repulsive interactions

Andressa Antonini Bertolazzo, Marcia C. Barbosa and M.M. Szortyka

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Water is the most important liquid for the existence of life in our world. It has a huge use in industry and life can exist at low temperatures only due to water's anomalous properties. Water anomalies are at accessible temperature ranges and because of that its anomalies are so important. A lot of models were created to simulate water, but what is necessary for a model to have anomalies is still a question. In continuous models, where the interaction of particles are described by an effective potential, some kind of water anomalies can be presented when the effective potential has a competition of two scales (one of them needs to have attractive interactions). In lattice models the structure is changed and the lattice make possible to have two competing ranges of interaction without attractive interactions. This work considers a two-dimensional model defined on a triangular lattice with a nearest neighbour hard core exclusion and a next-to-nearest-neighbors finite repulsive interaction. This model, that has only repulsive interaction, can reproduce some water anomalies such as density and diffusion anomalies.

11. A Unifying Motif of Intermolecular Cooperativity in Protein Associations

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When examined at the molecular level, most biological processes entail protein associations. In thermodynamic terms, the binding process relies on a small fraction of interfacial residues called hot spots. As shown in this paper, these hot spots share a unifying molecular attribute: they provide a third-body contribution to intermolecular cooperativity. By intermolecular cooperativity we mean three-body interactions defined by two purely combinatorial rules based solely on structural analysis of protein complexes: a) one body belongs to a protein chain and the other two, to its binding partner, b) two of these bodies are paired by an (intra or intermolecular) electrostatic interaction whose dehydration is promoted by nonpolar groups in the third body. This characterization does not preclude the third body from being also engaged in an intermolecular hydrophobic interaction. Intermolecular cooperativity is essential to maintain the integrity of the protein-protein interface by preventing disrupting hydration of interfacial polar moieties. The molecular attribute characterizing the hot spots can be exploited in rational drug design since such regions may serve as blueprints to engineer small molecules disruptive of protein-protein interfaces.

12. Temperature dependence of the structure of protein hydration water and the liquid-liquid transition

Sebastián Roberto Accordino, David Cesar Malaspina, J. Ariel Rodriguez Fris, Laureano Alarcón and Gustavo Appignanesi

Universidad Nacional del Sur, Argentina

We study the temperature dependence of the structure and orientation of the first hydration layers of the protein lysozyme and compare it with the situation for a model homogeneous hydrophobic surface, a graphene sheet. We show that in both cases these layers are significantly better structured than bulk water. The geometrical constraint of the interface makes the water molecules adjacent to the surface to lose one water-water hydrogen bond and to expel the fourth neighbours away from the surface, lowering local density. We show that a decrease in temperature improves the ordering of the hydration water molecules but preserving such geometrical effect. For the case of graphene, this favors an ice Ih-like local structuring, similarly to the water/air interface but in the opposite way along the c-axis of the basal plane (while the vicinal water molecules of the air interface orient a hydrogen atom towards the surface, the oxygens of the water molecules close to the graphene plane orient a lone pair in such direction). In turn, the case of the first hydration layers of the lysozyme molecule is shown to be more complicated, but still displaying signs of both kinds of behavior, together with a tendency of the proximal water molecules to hydrogen bond to the

protein both as donors and as acceptors. Additionally, we make evident the existence of signatures of a liquid-liquid transition (Widom line crossing) in different structural parameters at the temperature corresponding to the dynamic transition incorrectly referred to as "the protein glass transition".

13. Wrapping mimicking in drug-like small molecules disruptive of protein–protein interfaces

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The discovery of small-molecule drugs aimed at disrupting protein–protein associations is expected to lead to promising therapeutic strategies. The small molecule binds to the target protein thus replacing its natural protein partner. Noteworthy, structural analysis of complexes between successful disruptive small molecules and their target proteins has suggested the possibility that such ligands might somehow mimic the binding behavior of the protein they replace. In these cases, the molecules show a spatial and ‘‘chemical’’ (i.e., hydrophobicity) similarity with the residues of the partner protein involved in the protein–protein complex interface. However, other disruptive small molecules do not seem to show such spatial and chemical correspondence with the replaced protein. In turn, recent progress in the understanding of protein–protein interactions and binding hot spots has revealed the main role of intermolecular wrapping interactions: three-body cooperative correlations in which nonpolar groups in the partner protein promote dehydration of a two-body electrostatic interaction of the other protein. Hence, in the present work, we study some successful complexes between already discovered small disruptive drug-like molecules and their target proteins already reported in the literature and we compare them with the complexes between such proteins and their natural protein partners. Our results show that the small molecules do in fact mimic to a great extent the wrapping behavior of the protein they replace. Thus, by revealing the replacement the small molecule performs of relevant wrapping interactions, we convey precise physical meaning to the mimicking concept, a knowledge that might be exploited in future drug-design endeavours.

14. Water confined in model hydrophobic cavities and tunnelsand carbon nanotubes

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Through molecular dynamics simulations we analyze the behavior of water in contact with model hydrophobic cavities and tunnels. We study the hydration and filling propensity of cavities and tunnels carved in monolayers of alkanes and single-wall carbon nanotubes of similar size. Our results determine the dependence of the filling propensity according to the size of the cavity, showing the dynamic nature of the process. We compare the minimum diameter of solvation in the tunnels carved into monolayers with the diameter of carbon nanotubes and found that the diameter of the first ones is approximately twice compared with the minimun solvatation diameter of the carbon nanotubes, showing a more hydrophobic behavior. It also discusses the existence of water-water hydrogen bonds inside the hydrophobic cavities, which is a necessary condition for penetration into them.

15. Structure and dynamics of proton solvation in water-acetone mixtures

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Proton transfer is an ubiquitous phenomena and it is of paramount relevance in solutions chemistry. In aqueos solution, proton diffusion is controlled by the well-known Grotthuss mechanism, which is intimately related with the dynamics of hydrogen bond. This mechanism considers not the individual diffusion of a tagged proton, but a translocation of the average position of the excess charge which requires succesive spatial rearrangements along chains of hydrogen bonds. In this poster, I will present an analysis of the modifications that take place in the solvation structure and in the proton transfer dynamics for different water-acetone mixtures, covering almost all of the concentration range. Our analysis will be based on results from MD experiments using a multistate empirical valence bond Hamiltonian model that naturally includes a proton translocation mechanism. Our results predict a stabilization of the solvated Eigen cation [$H_9O_4^+$] at lower water molar fractions, in detriment of the symmetric Zundel dimer [$H_5O_2^+$]. For every mixture studied, the average solvation structure in the close vicinity of the hydronium is characterized by three hydrogen bonded, acceptor water molecules. Characteristic times for the proton translocation jumps have been computed using population relaxation time correlation functions. Compared to the pure water results, the rates at low water molar fractions fall down up to one order of magnitude. The proton diffusion is also drastically reduced, reaching values which are three times lower than those obtained for pure water.

16. Computational Design of Mesoporous Silica for CO_2 sequestration: controling nanoconfined supercritical fluids.

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An understanding of the phenomena of interface and transport of ions and molecules (H_2O and CO_2) in confined geometries is crucial, especially in the context of CO_2 sequestration. Atomistic calculations can provide interesting ways to address these issues. Here, we apply molecular dynamics calculations to study the effects of confinement on the wettability and transport phenomena of CO_2 within SiO_2 mesostructures. Knowing the effects of nanoconfinament of CO_2 in silica can lead to production of mesostructures "tailored" to optimize the specific separation and CO_2 capture. We started from extensive silica amorphous (106 atoms) to generate mesoporous structures. Voids have been created within this matrix, minimizing the surface area and pore energy. Optimizing the radius and geometry of the voids, we can generate any topology and sub-networks of pores embedded in the matrix. The porous were filled by supercritical CO_2 under different thermodynamic conditions (T=300K and pressure range of 50 to 500 atm). In this first phase, channels has been modeled with three forms of ellipsoids joined two by a reduction in diameter at the center, an ellipsoid and a cylinder. Our MD calculations indicate that the radial function of pairs decreases with increasing pressure and an accumulation of CO_2 near the surface. The surface tension increases as the pressure increase (from 0.92 to 0.96 N/m) and the diffusion coefficient was found to be lower in the channel at a reduced diameter in the center and decreases from the interface to the channel's center.

17. The oxide gold anodically grown on the confined aqueous layer bounded by the water/ anisol interface

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Preliminary work for the captive drop of an organic liquid immersed in the aqueous environment on the gold surface, shows that the contact angle is very close to 0o. The surface of gold electrodes in the double layer and in the gold oxide regions are investigated at pH 7 in confined phosphate buffer aqueous solutions and in 0.5 M HClO4 using Contact Angle (CA), Voltammetry, and Electrochemical Impedance Spectroscopy (EIS) techniques. Different experiments are performed using Benzene, Toluene, Anisol, Hexane, m-Xylene, Choroform and Butylacetate [1] developing different external water/solvent interfaces. The EIS results for the electrode in contact with solvents are similar to that observed in the absence of solvent. The capacity value is similar in the double layer region and at 1.7 V vs SHE for the first minutes of the oxide monolayer growth. For longer times at 1.7 V a second time constant rises at lower frequencies

showing the effect of the different solvents on the oxide layer aging. Particularly an increase of the contact angle is also noticed in contact with anisol. These effects point to an increase of the surface heterogenity induced by either the oxide growth and aging or the lifting of the surface reconstruction in the water double layer region similar to that reported for Au(100): hex  (1x1). The capacity measured are similar to that observed in the gold/electrolyte interface, showing that several layers of water remain on the cycled gold electrode after the addition of the organic solvent.

18. Themodynamic and Dynamic anomalies in water in porous media

Alexandre Penteado Furlan, Eduardo Fiore dos Santos, Marcia C. Bernardes Barbosa

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Water exhibits thermodynamic, dynamic and structural anomalous properties when compared with other substances. While most liquids contract upon cooling, water expands below T = 4ºC at ambient pressure, which characterize the densit anomaly. Recently, confined water has been receiving a lot of attention due the its applications in industrial and biological systems. In this work, we study the effects of a confinement of a water-like model in random porous media by two different approaches. First, we employ molecular dynamics simulation in the canonical ensemble. The system exhibits two types of interactions: a particle-particle and a particle-porous. In the particle-particle interaction a two length scale effective potential with repulsive shoulder at $r/\sigma_{particle} \approx 1$ *and very small attractive part around* $r\sigma_p \approx 3.8$ *is used and the particle-porous interaction is given by a Weeks-Chandler-Andersen (WCA) potential. In the second approach employs a two-dimensional lattice model defined on a triangular lattice in the grand-canonical ensemble. This model has nearest neighbour interactions given by short-range and hydrogen-bonds energies. Using molecular dynamics simulation, we analyse the influence of the random porous media in the structure of the system through the radial distribution function and the changes in the pressure-temperature phase diagram. In the Monte Carlo simulation we analyse density-chemical potential phase diagram and the number of hydrogen bonds per site.*

19. Structural and dynamic behavior of atomistic water models in the supercooled regime

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Several atomistic water models reproduce the properties of water reasonably well at ambient conditions. However, at lower temperature the simulations results show discrepancies with some of the properties observed experimentally. Most notably, no spontaneous crystallization is observed even at large degree of supercooling. In this work we present a systematic study of the supercooled regime using a variety of models, including TIP4P-Ew, TIP4P-2005, TIP5P-Ew and Six-Site. We found that all the models show the same qualitative picture characterized by a maximum in the heat capacity followed by a dramatic kinetic slowdown as the temperature decreases even further. These results are consistent with a liquid-liquid phase transition in the metastable regime, as suggested by several authors. After comparing the diffusion coefficient of the different models with the experimental values using a rescaled temperature, we conclude that the TIP5P-Ew produces the better description of supercooled water. Finally, we use this model to quantify the cage effect by the distribution of mean square displacements of the water molecules, the hydrogen bond and cage self correlation functions obtaining the characteristic time scales of relaxation for different supercooled temperatures.

20. Nuclear Matter at low temperature and density: A case study of frustration in a two component fluid

Claudio O. Dorso, Pedro A. Giménez Molinelli and Juan I. Nichols

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Nuclear Matter is an ideal system comprised of two types of particles: 'Neutrons' and 'Protons'. The interaction is such that particles of the same type have a purely repulsive potential (Soft Spheres-like) while particles of differt type present a Lennard-Jones like potential, with a short range attractive part. We describe a purely classic interaction model which presents all these characteristics. Using molecular dynamics simulations with this model, we study the behavior of Symmetric Nuclear Matter (system with the same number of 'protons' and 'neutrons') under periodic boundary conditions for a wide range of densities and temperatures. We observe that, for low enough temperatures, there is a critical density below which the system relaxes to non-uniform, compact structures. Allegedly, these structures arise from a frustration of a volume energy term by a surface term.

21. Grand Canonical -Molecular Dynamics simulations of sorption isotherms in Nanopores

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We focus on the development and implementation of a hybrid, Grand Canonical Monte Carlo - Molecular Dynamics, method for a variety of potentials in Mesoporous materials to obtain adsorption isotherms which can reproduce the hysteresis commonly seen in these systems. With this approach we can sample the dynamical properties of the system (Molecular Dynamics), without loosing the Grand Canonical properties (Monte Carlo). We use LAMMPS as our main tool, a versatile program to perform molecular dynamics, to which we have added a Grand Canonical Monte Carlo subroutine in the main input script. We validate our implementation against previous Monte Carlo results in a simple system consisting of a fluid in a slit pore interacting via Lennard-Jones potentials. The main feature to be adjusted in this scheme is the ratio between the Monte Carlo and the Molecular Dynamics steps: we present how such ratio influence the outcome of the simulations, and the resulting isotherm for the optimized ratio. We also present results of this method to obtain sorption isotherms of water in pores of different geometries.

22. Viscosity and diffusion in supercooled glycerol-water mixtures

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The viscosity of supercooled glycerol aqueous solutions, with glycerol mass fractions between 0.70 and 0.90, have been determined to confirm that the Avramov-Milchev equation describes very well the temperature dependence of the viscosity of the binary mixtures including the supercooled regime. Chronoamperometric measurements with cylindrical microelectrodes were also used to investigate the diffusion of ferrocene methanol in super-cooled glycerol aqueous solutions over a wide range of viscosity (1.5×10^{-3} – 1.5×10^{2} Pa.s) and reduced temperature ($0.50 < T_g/T < 0.78$). Diffusion-viscosity decoupling was observed at $T_g/T \approx 0.65$, being the diffusion coefficient of the probe close to the glass transition temperature much higher than that predicted by the hydrodynamic Stokes-Einstein model. Contrary to the observed dependence on concentration of the reduced temperature onset of the decoupling for the diffusion of glycerol in glycerol-water mixtures, the onset of the decoupling of ferrocene methanol in the same mixtures seems to be independent on the mixture composition. A critical analysis of the viscosity data of the mixtures in the supercooled region allowed us to reconcile both results.

23. Free volume/percolation model for the glass transition temperature of polyols aqueous solution

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The glass transition behavior of aqueous solutions containing carbohydrates or natural biopolymers is fundamental to determine their stability during storage of biomolecules, cells or organisms at low temperatures and the damage of the materials being cryopreservated. We use the free volume/percolation model (FVPM) that relates T_g to the percolation threshold of a 3-dimensional system, to estimate the glass transition temperature of simple polyol-water systems and compare the results with the experimental values and those obtained with other theoretical and semiempirical models. The model requires no adjustable parameters, but only information on the volumetric data of the aqueous system. Once the molar volume of water in the supercooled region was calculated by using the trehalose-water mixtures as a model system, a validation of the model was attempted by comparing its prediction with experimental data for other polyol-water systems. We have chosen aqueous solutions of polyols for which volumetric data are available, such as sucrose, fructose, glucose and glycerol.

24. Allosteric regulation, the role of the unprotected hydrogen bonds

Joan Manuel Montes de Oca, J. Ariel Rodriguez Fris and Gustavo Appignanesi

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At present, the complex mechanisms that govern protein interactions and enzymatic regulation remain poorly understood. In this work, using computational analysis of protein coordinates obtained from the Protein Data Bank, we found evidences that such kind of problematic could be resolved taking into consideration three bodies interactions, two bodies for protein backbone hydrogen bonds (HB) and the third body for carbonaceous (carbon atoms in residues not bonded to N, O, P, S) around this HB. In the particular case of 3-phosphoinositide dependent protein kinase-1 (PDK1), the ability of ligands to shield or "wrap" dehydrons (HBs not sufficiently protected from water by carbonaceous) in the allosteric domain of the enzime was analyzed. The ligands induce morphological changes in the enzime, so we followed the variations in the dehydron pattern in the catalytic domain of the enzyme to justify its activity. The results obtained from this theoretical approach could help in the understanding of the relationship between the enzime structure and action of drugs (the keystone in drug design) and the way in which enzymes operates.

25. Experimental verification of democratic particle motions by direct imaging of glassy colloidal systems

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We analyze data from confocal microscopy experiments of a colloidal suspension to validate predictions of rapid sporadic events responsible for structural relaxation in a glassy sample. The trajectories of several thousand colloidal particles are analyzed, confirming the existence of such rapid events responsible for the structural relaxation of significant regions of the sample, and complementing prior observations of dynamical heterogeneity. Thus, our results provide the first direct experimental verification of the emergence of relatively compact clusters of mobility which allow the dynamics to transition between the large periods of local confinement within its potential energy surface, in good agreement with the picture envisioned long ago by Adam and Gibbs and Goldstein.

26. Neutron scattering kernel for light and heavy water including structure and molecular diffusion

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The thermal neutron scattering kernels available for nuclear engineering applications in ENDF format over-predict the values of the total neutron cross sections in the cold energy range up to 100% and fail to reproduce the features observed by QENS and neutrondiffraction. These scattering kernels are based on only two essentially different models which contain a rough representation of the isolated molecule's dynamics, do not include collective vibrational modes or molecular diffusion, and do not consider the details of water structure. At the Neutron Physics Group of Centro Atómico Bariloche we are developing new scattering kernels for light and heavy water that include a better representation of cold neutron interactions using the standard numerical tool LEAPR/NJOY. In this poster we will present some results obtained by explicit inclusion of molecular diffusion and in the translational contribution to S(Q,w) for each liquid, as well as the coherent effects in the case of heavy water.