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Solubility of Propene in Polypropylene from Gibbs Ensemble MC Simulation and PC-SAFT EOS

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Influence of propylene tacticity and molecular weight on solubility of propene in isotactic and atactic polypropylene is investigated using Gibbs ensemble Monte Carlo simulation at constant temperature and pressure.

The mixture simulations were conducted in two coexisting simulation boxes. One of the boxes contained the polymer rich phase and the second contained the propene vapor phase. The NERD united atom force field was used to represent interactions in the mixture.

The solubility was determined at different temperatures, pressures and molecular weights and comparisons were made with available experimental data and predictions of the PC-SAFT equation of state. Structure of the mixture was investigated and correlation between propene and different parts of the polymer chain was evaluated using the radial distribution function.

Light propagation and scattering in liquid crystals with large-scale one-dimensional periodicity

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Propagation and scattering of electromagnetic waves, the field of a point source and the correlation function of the director fluctuations in helical liquid crystals with the large pitch are investigated. The wave propagation and the fluctuations spectrum are analyzed in the framework of unique approach based on the modified WKB method. The field of a point source, i.e. the Green's function, is constructed when the pitch is much greater than the wavelength of light.

The solution obtained contains two contributions associated with two types of waves, existing in an anisotropic uniaxial medium, ordinary and extraordinary. For the extraordinary wave at far distances there exists a forbidden zone, namely a restriction on possible directions of wave vectors. This effect is concerned with a turn of beams, due to variation of a refractive index along a beam. A capture of beams and formation of a plane wave channel takes place. It is shown, that the extraordinary beam does not lie in a plane.

The correlation function of the director fluctuations in cholesteric liquid crystals is constructed. The short wave fluctuations with the wavelength much less than the cholesteric pitch are considered. There are points where the interaction of fluctuation modes takes place. The general scheme for calculation of intensity of scattered light is offered. The angular and polarizing dependences of scattered light are calculated. In particular, it is shown, that intensity of scattered light depends on the sizes of system in unusual manner.

Computer Simulation Studies of an Amphiphilic Polymer at an Air-Water Interface

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1,2-Dimethoxyethane (DME) contains the two major dihedral interactions present in the polymer poly(ethylene oxide) (PEO) (C-0-C-C and O-C-C-0). Consequently, its conformational energies have been extensively studied experimentally and theoretically in both the gas and liquid phases.

This poster describes a combined quanturn mechanical ab, initio and classical. molecular dynamics study to calculate the conformations of DME in the gas and liquid and to extract a force field to model PEO. The latter has been used to carry out molecular dynamics studies of an amphiphilic polymer at a water-air interface.

In this work, the ten major conformations and two major barriers to rotation in DME, have been subject to ab, initio geometry optimisation at the MP2 and B3LYP levels of theory. The optimised energies were used to parameterise a force field for DME, which was refined by carrying out molecular dynamics simulations of DME in the liquid phase, in an attempt to obtain good agreement with experimental data.

The force field was subsequently used in an atomistic molecular dynamics simulation of an arnphiphilic graft-copolymer consisting of a polynorbornene backbone with PEO sidechains, sitting at a TIP4P water/air interface. At low surface coverage, in agreement with experimental observations, the polymer spreads out at the interface, but a small degree of penetration of the PEO chains into the bulk water is observed. At higher surface coverages the chains stretch down into the aqueous subphase forming a polymer brush.

Density profiles from these calculations were used to generate neutron reflectivity curves to compare with experimental. measurements.

Supramolecular periodic structures formed by rod-sphere aggregates

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We present the results of a series of MD and MC simulations investigating the phase behaviour of rod-sphere mixtures.

We model the rods as Gay-Berne particles and the spheres as Lennard-Jones particles and examine, in particular, the effect of changing the strength and symmetry of the rod-sphere interaction.

As well as finding straightforward demixing behaviour, we find, for some systems, microphase separation and even the formation of supramolecular periodic structures. The dynamics of these structures are examined, as are their responses to applied fields.

Chain Length Effect on the Structure of a Alkyltrimethylammonium Chloride Monolayer Between two Immiscible Liquids

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Surfactant monolayers and thin films have been extensively studied for more than a century. They display complex phase diagrams and behaviour [1] and are widely used in industry.

Extensive theoretical and experimental work has been performed for Langmuir and Langmuir-Blodgett interfaces and only recently a small number of studies have been performed on nonolayers between to immiscible liquids [2].

The knowledge of the relationship between the surfactant molecular structure and the macromolecular interfacial structure is important to understand and predict the performance of the surfactant. Yet, only recently the molecular behaviour of the monolayers could be obtained thanks to the advent of new experimental techniques like vibrational sum frequency generation spectroscopy, neutron reflection and second harmonic generation, among others. Relevant examples are the investigation of the detailed structure of the hydrocarbon tail [3] or the influence of the counter ion [4] on the behaviour of the monolayers.

In the present work we report a Molecular Dynamics simulation study of a alkyltrimethylammonium chloride (CnTAC) monolayer (n=8, 12 and 16) in the water/iso-octane interface at constant area per molecule.

A comparative discussion on the chain length is made, allowing us to gain some insight into the structure and dynamics of the simulated systems at the molecular level, which is very difficult to access from experiment.

Our results are also compared with available experimental results, namely the surfactant tail conformations and orientations, surface roughness and monolayer width.

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Ordering in Liquid Crystal Droplets for Scattering Polarizer Applications

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We report on a comprehensive study to measure the interactions between polymer and liquid crystal droplets for the application of polymer dispersed liquid crystal (PDLC) scattering polarizers.

As tensile strain is applied to the PDLC, an optical polarizer element is created.

Using solid state nuclear magnetic resonance we report on the degree of orientational order at the droplet wall interface as a function of strain and these can be correlated to optical measurements.

Predictions of molecular chirality and helical twisting powers

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When a nematic liquid crystal is doped with a low concentration of chiral solute molecules a chiral nematic phase is induced in the system. The helical twisting power, ~m, of a chiral dopant is a measure of the twist the dopant is able to induce in a nematic phase. The ability to predict accurately the helical twisting power (ITTP) of chiral dopant molecules is of fundamental theoretical interest in molecular chirality, as well as having useful technological applications in the design of new materials with high HTPs.

The work presented here concentrates on quantitative measurements of molecular chirality based purely on the molecular shape of the chiral dopant. The scaled chiral index [1,2] and the chirality order parameter' have shown good agreement with experimental HTPs for a variety of chiral dopant molecules. We have also undertaken a study of a number of chiral molecules using a molecular Monte Carlo simulation approach coupled with calculations of molecular chirality based on the chirality order parameter.'

Results for a variety of TADDOL derivatives show good agreement with experimental findings for the sign, magnitude and the temperature dependence of the HTP. For a photochromic chiral dopant with variable HTP we are able to model the reduction in the HTP when photoisomerisation occurs. Our studies on a liquid crystalline material with a single chiral centre have reproduced a temperature dependent twist inversion in the material.

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Molecular size and local stiffness of molecular bottle brushes by Monte Carlo simulations

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Molecular bottle brushes are densely branched comb polymers that may typically carry a side chain every backbone monomer. Such molecules are promising templates for the construction of gold nanowires, and may form ordered domains thanks to an enhanced backbone stiffness that can be tuned by suitably modifying the side chains.

Here we report some recent results obtained through Monte Carlo computer simulations. We use a coarse-grained bead and spring model, where the beads are connected by ideal springs and experience only hard-sphere excluded-volume interactions. We model bottle brushes carrying one side chain every one or two backbone beads (low- and high-density bottle brushes) in comparison with linear chains of the same backbone length n_b (up to 100 beads). In all cases, the molecular size shows a power-law dependence on n_b for a fixed arm length.

In particular, the Flory exponent for the backbone mean-square end-to-end distance $<R_b^2>$ of bottle brushes increases significantly above ν_R = 0.588(2) of linear chains (for instance, we get 0.71(1) for 5-beads arms). On the other hand, $<R_b^2>$ increases to a constant value upon increasing the arm length at a fixed backbone size. We also calculate the probability distribution function $g(R_b)$ for the backbone end-to-end distance: For all polymers we find an excellent fit with the function $g(R_b)$ = $A\cdot\hat{R}_b^{\vartheta}\exp\left(-B\cdot\hat{R}_b^{\delta}\right)$, where $\hat{R}_b = R_b \Big/ \left\langle R_b^2\right\rangle^{1/2}$. Interestingly, ν_R obtained from $\delta = (1 - \nu_R)^{-1}$ is in good agreement with the former figures.

Finally, we discuss the apparent persistence length l_{pers} of the backbone and the aspect ratio l_{pers}/D, the molecular diameter D being taken as twice the mean-square end-to-end distance of the arms. Due to the excluded-volume interactions, , l_{pers} increases with the backbone length at a fixed arm size, but it is much larger in bottle brushes than in linear chains.

Molecular Modeling of L-Lysine adsorption on silica surfaces.

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Molecular modeling techniques, semiempirical quantummechanics and force fields, were used to investigate molecule-molecule and molecule-substrate interactions of L-lysine molecules in aqueous solution with a hydrophilic silanolic surface and with a hydrophobic methylated surface.

The system was simulated at the amino acid's isoelectric pH (9.5) by introducing a negative charge on the silanolic surface and using the predominant lysine forms at this pH, i.e. neutral zwitterionic form and diprotonated form.

Both semiempirical and FF calculations indicate the strong interaction between the e-protoned amino group of L-lysine with the surface, and the preferred orientation of the molecule with respect to the surface.

Statistical analysis of the system trajectories reveals that lysine molecules change the hydrogen bonding pattern of water. Water molecules play a substantial role in the studied interactions with the layer in proximity to the substrate and the amino acid.

Flow Properties of Nematic Polymers Studied by Dissipative Particle Dynamics

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Efficient computational treatments of non-equilibrium properties of nematic phases are mainly based on Leslie-Ericksen (LE) equations. Transient director patterns can be obtained by solving numerically LE equations using finite differences or finite elements discretization techniques. This approach often requires significant computational resources, especially when treating highly viscous fluids (nematic polymers) and/or complex geometries. As an alternative, we explore in this study an implementation of dissipative particle dynamics (DPD) [1] for anisotropic fluids. DPD is a particle?based simulation methodology, which integrates a consistent description of thermal stochastic fluctuations and their effect on rheological observables, currently employed for the description of colloid and polymeric fluids [2],[3]. In order to apply a classical DPD approach to the study of polymeric mesophases some additional features are introduced, such as:
1) a coarse-grained description of the internal flexibility of the polymeric chain [3]; 2) an effective parameterisation of the orientational order of segments in the chain (main-chain nematic polymers) or lateral linked segments (side-chain nematic polymers). In this work we discuss alternative choices of orientational potentials and we present simulations for standard rheological set-ups.

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Density functional and ab initio studies on the molecular structures of the homologous series of P,P'-alkylcyanobiphenyls

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The molecular structures of pentyl, hexyl, heptyl, and octyl cyanobiphenyls have been studied using ab initio (HF and MP2) and hybrid density functional (B3LYP) methods.

Harmonic frequencies, absolute infrared intensities, Raman scattering activities, dipole moments and rotational constants have been calculated at all the three levels of theory.

The theoretical results are compared with the available experimental data and other calculations reported earlier.

Monte Carlo simulations of Gay-Berne liquid crystal systems

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First part of this work includes determination of phase diagram of ideally alligned Gay-Berne liquid crystal with Monte Carlo and Local Density Functional methods and comparison of the results achieved by these tools.

In the second part structures of ideally alligned polar Gay-Berne liquid crystal are investigated by means of single point, two point and triple point distribution functions.

The third part is focused on examining correlations of symmetric and traceless alignment tensors in the isotropic phases of GB chiral liquid crystal.

Interactions between Spherical Colloids Mediated by a Liquid Crystal: a Molecular Simulation and Mesoscale Study

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Monte Carlo simulations and dynamic field theory (DyFT) are used to study the interactions between dilute spherical particles, dispersed in nematic and isotropic phases of a liquid crystal. A recently developed simulation method (expanded ensemble density of states, ExEDOS) was used to determine the potential of mean force (PMF) between the two spheres as a function of their separation and size. The PMF was also calculated by a dynamic field theory that describes the evolution of the local tensor order parameter.

Both methods exhibit an overall attraction between the colloids in the nematic phase; in the isotropic phase, the overall attraction between the colloids is much weaker, whereas the repulsion at short range is stronger. In addition, both methods predict a new topology of the disclination lines that arises when the particles approach each other. At separations comparable to the width of the molecular layers on the particles' surface, the two methods yield different defect structures. We attribute this difference to the neglect of density inhomogeneities in the DyFT.

Columnar and interdigitated structures from discotic mesogens. A computer simulation study

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Discotics form a rapidly growing family of liquid crystals. The typical structure of a discotic is that of flat core with a certain number of chains attached [1]. The central core has been realized with a large variety of aromatic structures, starting in particular from the classic triphenylene and truxene ones, to include now superyines and a large variety of other moieties [2,3]. An interesting possibility is that offered by metallorganic compounds, where a suitable transition metal helps in organizing a set of ligands with an appropriate planar geometry [4]. This increasing freedom and flexibility in the choice of structures allows the possibility of selecting cores and inserting groups that confer to the molecule properties of interest in view of applications, such as charge transfer ability or a suitable electrostatic moment.

We have modelled the discotic mesogen using a Gay Berne [5] attractive-repulsive potential without dipoles and with a set of two and three embedded dipoles located at selected positions in the molecular plane, to examine their overall molecular and dipolar organization. We have employed Monte Carlo (MC) simulations to investigate several temperatures corrisponding to nematic and columnar liquid crystal phases in the isobaric-isothermal (NPT) ensemble, paying attention to the characterization of the low temperature phase, that is found to be particularly sensitive to the dipolar configuration.

The simulations show that a system of apolar Gay-Berne discotic particles can form nematic and hexagonal columnar mesophases. Adding two symmetric and planar dipoles has the effect of destabilize the columnar ordering, in favour of a fully interdigitated arrangement of the molecular stacks, with strong correlations in the plane perpendicular to the director and large biaxiality. Finally, no columnar phase is observed for the systems with three planar dipoles up to very low temperatures.

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Computer simulation of liquid and solid benzene with different interaction potentials obtained from ab initio calculations.

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Computer simulation methods such as Monte Carlo (MC) and molecular dynamics (MD) have proven to be a powerful tool to study both liquid crystals and polymers materials, despite the computational problems due to the wide range of length and time scales involved. This latter feature, combined with the complex nature of the molecules forming these materials, has suggested to adopt rather simplified descriptions of the intermolecular interactions [1]. These models have proven valuable to study both the general structure-property relationships and the basic features responsible of the macroscopic behaviour.

At the same time their simplicity becomes a drawback when the interest focuses on a specific material, with a well defined molecular composition. The impressive development of the computational resources is making increasingly feasible to adopt atomistic models [2] for some smaller molecules. However a detailed representation of most liquid crystal and polymer forming molecules is not yet possible. Thus, in the construction of model potential functions, the problem becomes to find a good compromise between an accurate description of the specific molecular interactions and a reasonable computational cost.

With this aim, we have recently [3] proposed a method that allows the computation of intermolecular potential energy surface (PES) of large molecules from ab initio calculations. Once the PES is obtained, a fit using a model of the desired complexity can be performed.

In the present work the PES of the benzene dimer is ab initio calculated and fitted to three models of different complexity: a single-site Gay-Berne potential with a point quadrupole (GBQ model), a single-site S-function potential (S model) and an atomistic representation (FA model). The three model potentials are employed in MC and MD simulations and the results compared between them and with the experiment.

The goals of this work are to test both the reliability of the ab initio calculations through a very realistic model, and the capability of simpler models to reproduce macroscopic behaviour.

Moreover, considering the ubiquity of the benzene molecule in mesophase and polymer forming molecules, the simpler models are intended as a 'building block' to be used in hybrid models [4] of much larger molecules.
Different thermodynamic and dynamic properties, have been calculated in MD simulations using the FA model. Among them the second virial coefficient, the intermolecular pair correlation function and the diffusion coefficients yield a very good agreement with the experiment. Also the melting temperature is close to the experimental phase transition value.

The MC results with the single-site models, though not as close to the experiment as the FA ones, were satisfactory and call for further study in hybrid models. Between the GBQ and the S model, the latter seems to yield the better results.

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New Symplectic Method for MD Integration

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The Split Integration Symplectic Method (SISM) for molecular dynamics (MD) integration is presented. The fundamental idea of the SISM is to split the total Hamiltonian of the system into two parts each of which can be efficiently computed.

We propose to split the total Hamiltonian into a pure harmonic part that includes the harmonic terms of the total Hamiltonian, and the remaining part. The pure harmonic part of the total Hamiltonian is integrated analytically by means of normal mode analysis, and the remaining part is integrated numerically using a second-order leap-frog Verlet integration scheme.

The presented method was tested on systems of linear chain molecules, water molecules, and hydrogen peroxide molecules. The numerical results indicate that the integration time step used by the SISM is significantly larger than possible by standard methods.

The torsion potential of oligothiophenes: high-level quantum chemical study and interepretation of substitutent effects

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We have carried out a systematic ab initio study of the torsion potential of alpha,alpha'-bithiophene, using a range of electron correlation methods in combination with medium- and high-quality Gaussian basis sets.

Our MP2/aug-cc-pVTZ potential energy curve compares favourably with the available experimental data and was used in our molecular dynamics simulations of oligothiophenes.

We also address the question of the size-dependence and transferability of this potential to higher ologomers, by calculations on ter- and tetrathiophene.

Finally, we have studied the effect on the potential produced by several substitutents attached in the beta positions. The topological analysis of the molecular electron densities reveals the critical role played by specific surfur-heteroatom non-bonded interactions.

Molecular dynamics simulations of tetrathiophene crystals and thin films

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We present classical molecular dynamics simulations of the crystalline polymorphs and of thin films of tetrathiophene.

The crystal simulations reveal different degrees of molecular mobility in the polymorphs, and provide at the same time a critical test of the representation of intermolecular interactions by the empirical force field.

Simulations of 8-24 tetrathiophene molecules deposited on a graphite surface of 800 Angs^2 reveal the formation of a relatively ordered first layer, with the other layers above it being instead much more disordered.

Finally, we also present some results on the structure and dynamics of selected surfaces of the crystalline polymorphs.

NMR Line Spectra from Lattice Spin Models of Polymer-Dispersed Liquid Crystals

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We analyze the dynamical aspects of molecular ordering in nematic droplets with radial and bipolar boundary conditions --- as encountered in polymer dispersed liquid crystals --- by calculating and interpreting the corresponding 2H NMR spectra. In particular, we focus on effects of molecular motion like fluctuations of molecular long axes and translational diffusion, and on external field ordering effects.

Equilibrium configurations inside nematic droplets are obtained from Monte Carlo simulations of the Lebwohl-Lasher lattice spin model.

The effect of chain stiffness on the partitioning of polymers into pores

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We investigated the effect of chain stiffness on the partitioning of polymers into pores in good and theta solvents using coarse-grained Monte Carlo simulations. The solvent was not included in the model directly; rather a potential e_s representing the quality of solvent was used.

Stiffness was described as an energetic penalty for gauche over trans bonds. In the good solvent case with $e_s=0$ stiffness was used independently, and in the theta solvent case it was correlated with e_s. Confinement was provided by two hard parallel walls, with or without adsorption interaction.
From single chain properties, it was clear that chains behave as coils globally and do not reach the rigid rod limit. In partitioning into pores at low concentration, the size of the molecules is the important factor.

At higher concentrations, the interplay between different factors becomes more important. These include solvent quality, stretching of the molecules and hence a better packing ability for stiffer chains, changes in the size of the molecules, and breaking of contacts between chains.

Some of these effects can be seen in concentration profiles or the decomposition of the free energy into entropy and enthalpy. When it comes to partitioning in a good solvent at higher concentration, there is no difference in the value of the partitioning coefficient between flexible and semiflexible chains. In the theta solvent, however, chains with higher values of stiffness enter the pore more easily than the more flexible ones in contrast with their behaviour at low concentration.

Mesoscale Lattices And Temporal Multiplexing in Liquid Crystal / Polymer Dispersions

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We demonstrate multi-beam holographic lithography and temporal multiplexing techniques to create complex two- and three-dimensional structures in holographic polymer-dispersed liquid crystal (H-PDLC) materials. H-PDLCs are a variant of PDLCs formed under holographic conditions. The holographic image is typically a two-beam interference pattern, resulting in an array of liquid crystal (LC) droplets and solid polymer planes that act as a Bragg grating. Applying an external electric field can reversibly erase the resulting refractive index modulation.

Using multi-beam holographic lithography, two-dimensional square lattices and three-dimensional FCC lattices have been created. The structures of the created lattices have been confirmed using a scanning electron microscope. We demonstrate the switchabilty of the lattices and tunablity of the photonic bandgaps upon application of an electric field.

Instead of simultaneously exposing a sample to multiple laser beams, we have developed a technique for creating complex structures by time-sequentially exposing the sample with multiple holographic configurations. By time-sequentially exposing the sample, two switchable reflection gratings are formed in a single film.

The reflectance of the resulting gratings is well controlled by the individual exposure time. The optical performance can be modeled using a 2x2 matrix method based on the reaction diffusion equation.

Intramolecular Correlation Functions and the Spectra of Crystalline Polyacetylene

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The spectra of trans polyacetylene have been obtained from Molecular Dynamics simulations. The good agreement with the available experimental data obtained in previous works [1,2,3] has aimed us to perform a detailed analysis of the influence on the spectra of stretching, bending and torsional forces. To this end a vibrational dynamics study has been made by using the Molecular Dynamics technique.
Time autocorrelation functions of bond lenghts, bending angles and torsional angles have been evaluated.

The Fourier transforms of such functions have been compared with the densities of states obtained both for carbon and hydrogen atoms. This comparison is aimed at investigating the microscopic origin of the peaks which appear in the densities of states.

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