

CCP5 ANNUAL MEETING - ORDER IN LIQUIDS

The annual meeting of CCP5 was held this year in Sheffield on the topic “order in liquids”. The abstracts of the talks and posters are presented below.

ORAL PRESENTATIONS

SURFACTANT SOLUTIONS

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Surfactants in solution self-assemble reversibly to form large aggregates. These may be either spherical micelles, locally cylindrical (wormlike) micelles, or else made of bilayers (vesicles, sponge phases...). Such systems show complex thermodynamics and flow behaviour with a variety of interesting static and dynamic phase transitions. Often, worthwhile information can be gained from models in which each surfactant occupies a small number (2–8) of bonds or sites. In contrast, truly microscopic level modelling is limited at present to questions involving small aggregates (or parts thereof) only. Here a feasible aim might be to predict parameters (such as elastic constants) which can then be fed into larger scale, phenomenological descriptions. As examples of the latter, we focus on two cases where a need for large-scale computation is apparent:

(1) The dynamical instability in entangled micellar systems under shear. Recent analytical predictions and experimental results will be presented and compared with a large scale numerical study [1] of the nonlinear flow equations in which the coarse-grained dynamics of the micelles is included by a Monte-Carlo algorithm.

(2) The role of defects in bilayer sponge phases. These are described by a lattice gauge model which ascribes a certain line tension to “edges” and “seams” in the bilayer. This connects smoothly with an Ising model in the limit of high line tensions (where the bilayer becomes a dividing surface); however, our understanding of the rest of the phase diagram remains very limited.

[1] X.-F. Yuan and N. Spenley, in progress

THE ESCAPE OF THE CRITICAL POINT

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Novel Monte Carlo simulation techniques make it possible to study the phase behaviour of complex liquids such as polymeric systems and mixtures of colloids. These systems differ from simple (atomic or molecular) systems mainly because the role of entropy is so much more important for the phase behaviour. In my talk I shall consider several entropic phase transitions. Of particular interest is the demixing transition that occurs when polymer is added to a colloidal suspension. Computer simulations allow us to predict how the phase diagram of these mixtures depends on the size ratio between polymers and colloids. Moreover, the simulations lead us to predict novel phase behaviour that has, thus far, not been observed experimentally.

LIQUID STRUCTURE AND ORDERED SOLVATION CELLS

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It is becoming recognised that the order imposed on a solvent by a solute can have important consequences in many situations. In particular, it is now being suggested that molecular recognition in biological systems (e.g. drug/receptor, or sweetness perception) have as much to do with the hydration structure of the molecules as with the chemical composition of the molecules themselves.

At present, direct probes of solvation structure are pushing the limits of experimental techniques. The problem is well suited to examination through computer simulations, but the development of analysis techniques for elucidating and interpreting the details of solvation effects is still in its infancy. Further, where simulations have probed solvation structure, their ability to link in with reliable experimental data has often been weak.

This talk will present the results of a combined simulation/experimental study of solvent effects on the circular dichroism (CD) spectra of various camphor derivatives in achiral solvents. CD is a chiral phenomenon, and no signal is generated for achiral species. By the same token, interactions with an achiral system should not alter the CD of a chiral species. Thus, for camphors in achiral solvents, any solvent influence on the camphor CD can only arise if the solute induces a chiral solvation structure, and so the phenomenon provides a direct probe of solvation structure. By combining the experiments with MD simulations using some extensions to existing structural

analysis techniques, it has been possible to develop a detailed understanding of the structure of the solvation shell around the camphors, and how this depends on the solvent used. The results have some implications for solvent control of chiral phenomena such as asymmetric syntheses.

DL_ POLY ON THE T3D

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The current CCP5 flagship project is the development and application of the general-purpose parallel molecular dynamics code DL_POLY. The code is purpose-built to run on parallel machines, and has been developed at Daresbury Laboratory by W. Smith and T. Forester. The talk will outline the basic principles of the code, and will give some illustrations of the large-scale simulations that have been performed on biomolecular and other systems over the last year. The DL_POLY project has an allocation of time on the 256-processor Cray T3D at the Edinburgh Parallel Computing Centre, and some of the timings and trial simulations done on the machine in the past two months will be described.

THE PROTEIN-SOLVENT INTERFACE

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The interaction of proteins with aqueous solvent is important for their stability, conformation, dynamics and thermodynamics. In order to study structural aspects of protein-solvent interactions, we have adopted a multi-faceted approach in which we have analysed the experimental solvent data from protein crystallography and compared these analyses with energy minimisation calculations using traditional and novel electrostatic potentials and with molecular dynamics simulations aimed at the study of peptide stability. In this talk, I shall focus on apolar hydration especially for alanine, phenylalanine and leucine residues using these three approaches, and describe not only the protein-solvent interactions but the solvent-solvent interactions around apolar residues.

MOLECULAR DYNAMICS SIMULATION OF TIME-RESOLVED SPECTRAL SOLVATION SHIFTS IN LIQUIDS

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Classical molecular dynamics simulations are performed for the system 7-amino-3-methyl 1,4 benzoxazine 2-one (AMBO) in methanol at room temperature. The time dependent spectral shift of the fluorescence is estimated from non-equilibrium simulations, in which the charge distribution of the solute in ground state configurations of the solution is suddenly changed to that of the excited state (vertical transitions), and the transition frequency is calculated while the solvent cage adapts to the new distribution. The shift occurs mainly before 500 fs, with little broadening, reaching an asymptotic value of around 2000 cm^{-1}

Comparison with the linear response theory of solvation shifts shows that it correctly describes the large solute-solvent system, despite the apparently large perturbation (change of dipole moment $\simeq 5\text{D}$). Comparison is made with the orientational and energetic dynamics of the pure solvent to ascertain to what extent the solvation shift is representative of the dynamics of the solvent. The initial spectral relaxation is non-gaussian, contrary to recently studied small solutes, but is well correlated with the orientational motion. The influence of the internal degrees of freedom of this large solute is also assessed.

PHASE EQUILIBRIA AND SURFACE TENSION OF MOLECULAR FLUIDS

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The search for methods and interaction potentials with which to study fluid phase equilibria has academic and technological interest. In this work we present molecular dynamics simulations to study the liquid-vapour interface of molecular fluids. The systems are located in a rectangular cell with liquid in the middle and vapour on the left and right, with periodic boundary conditions in the three directions. Site-site effective potentials are used to describe the interactions between molecules. Chlorine, CH_2F_2 and water are simulated. Water is simulated using the SPC/E potential and the Ewald technique is used for the long-range interactions.

The calculated properties are the orthobaric densities and the surface tension as a function of temperature. The orthobaric densities for the SPC/E water model are in better agreement with experimental data than those found with Gibbs ensemble for the SPC potential. We have shown that the differences are due to the different potential and not because of the difference in the simulation methods employed. The effect of long-range interactions on the surface tension of water is analysed in detail. Their inclusion is very important because the simulation is developed in a rectangular box. Excellent agreement with experimental results is found.

STRUCTURE AND DYNAMICS OF HARD ELLIPSOIDS

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The hard ellipsoid system is perhaps the most obvious generalization of the venerable hard-sphere model, and may serve as a reference system for molecular liquids in the same way as did hard spheres for atomic liquids. A programme of molecular dynamics and Monte Carlo simulations of hard ellipsoids has been in progress at Bristol for several years. This talk will review what we have learnt regarding the structure, single-particle and collective dynamics, and phase transitions exhibited by these systems.

A NEW METHOD FOR DETERMINING THE CHEMICAL POTENTIAL FOR CONDENSED MATTER AT HIGH DENSITY

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We apply a space-dependent external potential to the fluid such as to produce both a high density, virtually homogeneous, region and a low density, not necessarily homogeneous, region. We easily measure the chemical potential in the low density region by Widom's fictitious-particle-insertion method by computer simulation. By constancy of the chemical potential, the value is the same in the high density region, which is the difficult to measure directly by this or any other method. The method has been tested for Lennard-Jones fluids, for which independent values of chemical potential at high density are known. The method is quite general and can be used for molecular liquids, polymer melts, mixtures, etc.

LOCAL ORDER IN FLUID LIPID-BILAYERS

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The fluid lipid-bilayer component of cell membranes is a mesoscopic system consisting typically of the order of $10^8 - 10^{10}$ interacting molecules. In its capacity as an interacting many-particle system, the membrane sustains correlated dynamical modes and it may display cooperative phenomena such as static global phase separation and dynamical local heterogeneity on micro- and nano-scales of $10 - 1000 \text{ \AA}$. The microscopic manifestation of the cooperative modes consists in the formation of heterogeneous structures, such as lipid domains, that are dynamically maintained. The lipid domains may be seen as either lateral density fluctuations or compositional fluctuations. The macroscopic consequences of these fluctuations are anomalies in response functions, such as the specific heat and the lateral compressibility. Results from Monte models of planar lipid bilayers will be described and it will be shown how lipid domains and local structure arise under different thermodynamic conditions [1], [2]. It is proposed that the dynamically heterogeneous membrane states are important for passive and active membrane functions such as trans-membrane permeability, enzymatic activity and the in-plane aggregation of protein sub-units to functioning protein complexes. Membrane-associated functions may be manipulated by changes in the heterogeneous membrane structure that can be significantly altered in response to changes in compositional, thermodynamic, and environmental conditions. The diverse physical effects, and possibly some physiological effects of a variety of molecular compounds interacting with membranes such as cholesterol and drugs like anaesthetics, may be understood in terms of the ability of these compounds to affect and modulate the dynamic membrane heterogeneity.

[1] K. Jørgensen, M.M. Speretto, J.H. Ipsen, O.G. Mouritsen and M.J. Zuckermann, *Biochim. Biophys. Acta*, **1152**, 135 (1993).

[2] O.G. Mouritsen and K. Jørgensen, *Chem. Phys. Lipids*, in press (1994).

SWIFT-HOHENBERG RELATIONS FOR THE DYNAMIC INSTABILITIES IN MICRO-PHASE TRANSITIONS OF ASYMMETRIC BLOCK COPOLYMER MELTS

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Density functional theory provides a general method for calculating the free energies in an inhomogeneous complex fluid. The present extension to off-equilibrium mixtures of copolymer chain molecules is essentially a generalisation of the dynamic RPA method, along the lines pointed out some years ago by de Gennes and others. These are time-dependent Ginzburg-Landau models with non-local and highly non-linear functional relations between densities and interaction fields. The method applies to systems in which the diffusion phenomena are slow enough to ensure, at any given moment in time (on a coarse-grained mesoscopic timescale), a *unique*, history independent, functional linkage between density profile and chain conformation distribution.

We present a few examples of numerical analysis of micro-phase transitions in block copolymer melts by numerical integration of the (stochastic) non-linear partial differential equations. Various predictions are made. An interesting result is that in a quenched asymmetric block copolymer melt, a symmetric defect leads to symmetrically propagating unstable dissipative waves. When these waves interact, interference is severely restricted due to non-linear interactions. In contrast, the interaction between the dissipative waves leads to the induction of new *asymmetric* propagations. In some cases, the interactions between these second order waves may lead to third order waves of yet another character. These effects can be understood by comparison with type $I_s(\omega_0 = 0, q_0 \neq 0)$ pattern forming systems introduced in a recent magnificent review of pattern formation outside of equilibrium [1].

By means of some simple transformations of the original dynamic non-linear RPA equation, we derive a variant of the so-called Swift-Hohenberg equation. This equation was originally derived for pattern formation in hydrodynamic convection systems. The analogy leads to an amusing observation: experimental Raleigh-Bénard convection cells may provide effective natural simulation devices for the study of micro-phase formation in copolymer melts. This may seem a remote possibility, but it is clear that the Swift-Hohenberg equation points the way to efficient calculation methods.

[1] M.C. Cross and P.C. Hohenberg, *Rev. Mod. Phys.*, **65**, 851 (1993).

ORDERING BEHAVIOUR OF CHAIN MOLECULES IN MODEL SYSTEMS: MONTE CARLO SIMULATIONS

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We have carried out athermal Monte Carlo model simulations of long chain molecules with several constraints on a simple cubic lattice. Our special interest was to investigate the ordering behaviour of linear flexible molecules with variation of both head density ($0 < \Phi < 1$) and molecular length ($2 \leq s \leq 15$).

First we investigated the influence of the dimensionality on the ordering behaviour. Therefore the heads of the molecules are confined to move along the x-axis whereas the chain segments could move *i*) in a plane *ii*) in the first quarter space and *iii*) in the upper half space. For two segment molecules the exact analytical solutions for all head line densities agree with simulation results. The ordering behaviour varies qualitatively within these different geometric cases. In case *i*) the degree of order shows a minimum behaviour at medium head line density and tends to unity when the head line density approaches unity. In case *ii*) the degree of order behaves monotonously.

In the upper half space we investigated several flexible molecules of different topologies with heads confined to the plane $z = 0$. The order parameter for short linear molecules shows a minimum at medium head density.

The ordering behaviour of two-chain molecules with $s_1 = 10$ segments in the main chain and $s_2 = \{1, 2, 4, 6, 8\}$ segments in the side-chain has been investigated. The side-chain was connected to the second segment of the main chain. The degree of order varies with side-chain length: if the side-chain consists of one segment, the order parameter strongly decreases in comparison with molecules without a side-chain. In the cases of $s_2 = 4$ and more segments in the side-chain, the order parameter is higher than for linear molecules.

The ordering behaviour of molecules with anisometric heads has to be described by two order parameters: one for the flexible chains and the other for the alignment of the heads. At high densities the heads form domains with preferred directions.

Work is now being undertaken to investigate the effect of including attractive interactions and non-zero widths for the heads in the z-direction. It is also intended to investigate other molecular topologies.

COMPUTER SIMULATION OF SOME GAY-BERNE LIQUID CRYSTALS

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The talk will present some recent work on Gay-Berne models of liquid crystals. Some bulk systems in three and two dimensions will be examined and the resulting types of order and molecular organisations discussed. Gay-Berne systems confined to spherical and cylindrical cavities will also be investigated. In addition to the use of Gay-Berne systems in modelling, the effect of isotropic-nematic-smectic phase transformations on certain phenomena will be considered with the explicit case of Förster type energy transfer used as an example.

LOCAL CLUSTER DYNAMICS AND ORDERING IN SHEARED LIQUID MIXTURES

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The momentum transfer and the associated relative motion between an atom and its immediate surroundings in sheared dilute atomic mixtures are examined using non-equilibrium molecular dynamics. We examine the variation in the momentum transfer, velocity and force autocorrelation functions as the dilute species mass is varied. The computations have been carried out for several shear rates. We also investigate the behaviour of the elements of the diffusion tensor under mass and shear rate variation. The elements of the diffusion tensor are observed to be increasingly non-isotropic with increasing shear rate. A video has been prepared using the AVS system to visualise the evolution of the relative dynamics between an impurity atom and its surrounding near-neighbours. The variation in relative dynamics as the mass of the impurity atom is increased and as the magnitude of the shear field is increased is shown.

HYDROGEN BONDING IN AMPHIPHILIC SYSTEMS AND LIQUID CRYSTALS

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Simple model molecules of amphiphiles will be used to examine the effect of hydrogen bonding on the phase behaviour of these systems. Aqueous solutions of amphiphiles are examined in some detail with particular reference to re-entrant phase behaviour. In this case the approach of Wertheim for molecular association will be used to describe the free energy. In the case of liquid crystal systems the effect of hydrogen bonding on the isotropic-nematic phase transition is examined by combining the Wertheim and Onsager approaches. The stability of the smectic and columnar phase relative to the nematic phase for associating systems is examined with a bifurcation analysis.

MOLECULAR DYNAMICS SIMULATIONS OF LIQUID CRYSTALS ON THE CRAY T3D

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Molecular dynamics simulations of simple systems are often ideal candidates for parallelization. The main computational task of calculating the forces between pairs of atoms is an inherently parallel process, and a number of techniques exist for doing this efficiently on a range of different parallel computers. On the CRAY T3D a particular friendly environment for MD work exists. 256 DEC Alpha-processors are coupled to fast inter-processor communications providing the possibilities of long time-scale simulations of large systems, with a minimum of communication overheads.

For liquid crystal systems the T3D provides a useful means of tackling problems which would be intractable on most other machines. Large scale simulations are required to study the formation of defects and disclinations in nematic phases, the stability of smectic phases, the formation of biaxial chiral phases and the structure within polymer liquid crystals.

In this paper we present preliminary results of our liquid crystal simulations on the CRAY T3D. We discuss the efficiency of the algorithms used, the problems which arise in their implementation, and the range of problems which can be tackled. Initial results from simulations of chiral liquid crystals using twisted boundary conditions are presented.

VIEWS ON PARALLEL PERFORMANCE IN COMPUTATIONAL CHEMISTRY

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Parallel computing is ideal for the biggest computational tasks in quantum chemistry, protein modelling, crystallography and studies of condensed matter and disordered systems. Microprocessor technology has enabled many groups to increase their computational power merely by buying the latest workstations. The problem sizes grow to fit the equipment. A more aggressive approach is possible with scalable parallel computing where the equipment can be selected to fit the problems.

POSTER PRESENTATIONS

PARALLEL PROGRAMMING FOR HIGH PERFORMANCE IN COMPUTATIONAL CHEMISTRY

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Many parallel programs have been developed on the Daresbury Intel machines by CCP5 members. All of these can now be ported, without significant change, to any set of Unix workstations and any of the shared or distributed memory parallel supercomputers, using our Intel-to-pvm libraries. This includes Cray, DEC, HP, IBM, SUN, Silicon Graphics and Transtech PARAMID equipment.

We have ported three CCP5 codes, CASTEP, FUNGUS and PARION to our workstations and PARAMID with only 5 new lines to invoke our Intel library.

In many cases a group of workstations can give dramatic performance increases over one station. Our real life case does the iterative inversion of a large full matrix to solve a fluid flow problem. A large problem needed to use virtual memory on one DEC Alpha and was killed after 20 minutes. On a pair of Alphas the problem ran, in real memory, in 74 seconds.

Our machine independent toolset makes parallel code development quite straightforward. This was essential for us in handling so many different machines. The largest code we have handled had 180,000 lines of C and Fortran and was parallelised with about 400 new lines. Protein modelling codes spend about 95% of their time in one routine to evaluate the forces. Parallelisation is, therefore, almost trivial, requiring a few lines for the algorithm and a little more work for the protein setup.

In short, parallel programming can be very straightforward, large gains can be made on basic equipment, and the UK academic community now has many powerful parallel machines for the most massive problems. Details and demonstrations will be presented at the meeting.

MOLECULAR DYNAMICS SIMULATIONS OF HEXANE IN A GAY-BERNE FLUID

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Molecular dynamics simulations of a hexane molecule in isotropic, nematic and smectic phases are reported. The interaction between the solvent molecules is modelled using the Gay-Berne potential and the hexane-solvent potential is modelled as an explicit site-site interaction.

The conformational distributions are reported for a hexane molecule at a fixed temperature but at different densities in isotropic, nematic and smectic phases, and these are compared with the results from Monte Carlo simulations on an isolated molecule at the same temperature. The positions and orientations of the hexane molecule at each time step in the molecular dynamics simulations are used to calculate interproton dipolar coupling constants. These data are used to test the mean field models which have been applied with dipolar couplings obtained previously from nuclear magnetic resonance experiments to yield conformational distributions.

SIMULATION OF LIQUID CRYSTALS

M.P. Allen, J.T. Brown, C.P. Mason, M.A. Warren

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We present some new results regarding the effects of periodic boundary conditions on the director distribution in liquid crystal simulations. We also give details of our attempts to simulate two-phase coexistence between liquid crystal and vapour phases.

COMPUTER SIMULATION OF ANISOTROPIC SYSTEMS. THE COLUMNAR NEMATIC PHASE ?

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A necessary condition for a compound to form a mesophase is that its molecular shape must deviate from spherical symmetry, but molecular shape alone cannot determine whether a mesophase will be stable. Pure pentakis(phenylethynyl) phenoxydecane (D102) [1], for example, does not exhibit a liquid-crystalline phase. However, when doped with 2,4,7-trinitrofluorenone, which is also non-mesogenic, liquid-crystalline phases are induced. The reason why this phase induction occurs is not known. As there is a dramatic colour change on mixing, one possible explanation is that a charge transfer complex is formed, although charge transfer interactions are generally thought to be rather weak. Another possible explanation is that quadrupolar forces are important. In a pure system, these forces would tend to destroy face-to-face alignment between a pair of discs. However, in a mixture in which the components have opposite quadrupolar moments, face-to-face alignment between unlike molecules would be enhanced.

To investigate the role of quadrupolar forces in a system of disc-like molecules, we have undertaken a computer simulation study based on the Gay-Berne potential [2], which has proved to be of considerable value in understanding the behaviour of pure systems composed of disc-like particles [3]. We have added a point quadrupolar term to the potential to account for the electrostatic interactions. Two systems have been studied using this model potential

- (I) a pure system of Gay-Berne quadrupolar discs, and
- (II) a binary mixture of such discs, differing only in the sign of their quadrupole moments.

Both systems were investigated by Monte Carlo simulations at constant volume as a function of temperature. In system *I* the quadrupolar forces were found to destroy the usual columnar packing exhibited by a model disc-like mesogen with no quadrupolar interactions c , although there is an indication that a tilted columnar phase may have been formed. System *II* was found to exhibit, in addition to an isotropic and a nematic phase, a columnar phase in which the discs pack more-or-less alternately.

[1] K.Praefcke, D.Singer, M.Langner, B.Kohne, M.Ebert, A.Liebmann and J.Wendorff, *Molec. Cryst. Liq. Cryst.*, **215**, 121 (1992).

[2] J.G.Gay and B.J.Berne, *J.Chem. Phys.*, **74**, 3316 (1981).

[3] A.P.J.Emerson, G.R.Luckhurst and S.G.Whatling, *Molec. Phys.*, **82**, 113 (1984)

MOLECULAR MODELLING OF INHOMOGENEOUS BROADENING IN SOLIDS

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The inhomogeneous broadening of the optical transitions of a probe molecule in a solid at low temperature is caused by fluctuations of the host-matrix stabilisation in the close surroundings (20\AA), like short range repulsion, electric multipole interaction, dispersion forces and, in some cases, special forces like hydrogen bonding.

Estimation of inhomogeneous broadening thus poses two problems: calculation of the interactions for a given host-matrix configuration and proper accounting for the variety of configurations with suitable statistical weights. We approach this problem through molecular modelling. Molecular dynamics simulations supply the host-matrix configurations, including a large part of the intermolecular correlations present in the matrix because of steric effects or hydrogen bonding. A semi-empirical quantum calculation of the probe's spectrum, including the perturbation by the host molecules in each configuration, then yields the optical inhomogeneous lineshape.

INHIBITION OF THE CRYSTAL GROWTH OF NATURAL GAS HYDRATES

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Gas hydrates form and cause blockages in natural gas pipelines - so resulting in inefficiency in the flow of gas and producing a potential hazard if the pipeline were to become plugged by the crystalline gas hydrate. This work has investigated the potential use of a water soluble polymer, polyvinylpyrrolidone (PVP) to inhibit this. PVP has the interesting property of structure-ordering in liquid water and has freeze-preservation properties.

Monte Carlo calculations were used to study the adsorption of the polymer on the hydrate surfaces. Various tacticities of PVP were considered and the polymer conformational trends analysed for these calculations. Adsorption sites have been identified and PVP chains were shown to lie flat on the surface rather than at an angle to it. Therefore, an inhibition mechanism is proposed whereby the hydrate growth sites, at which water molecules would add to the hydrate lattice, are

covered by the polymer.

GENERALISATION OF THE GAY-BERNE POTENTIAL TO INCORPORATE HETEROGENEOUS PARTICLE-PARTICLE INTERACTIONS

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In this poster, we derive a generalised form for the shape parameter governing the pair interaction between ellipsoidal particles. This generalisation is obtained by considering the overlap of two arbitrarily (i.e. differently) stretched gaussians. An interaction potential for heterogeneous particles is then obtained by importing this shape parameter into the standard Gay-Berne form. A parameterisation of this potential is obtained for a rod-disk interaction.

A COMPUTER SIMULATION OF THE MICROSTRUCTURE OF A PARTICULATE DISPERSION

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We report on a computational simulation of a dispersion of iron particles undertaken to study the influence of the magnetostatic interactions on the microstructure of a particle ensemble. The simulation considers an equilibrium state derived from an initial random state by the force-bias Monte Carlo technique. We have studied a three dimensional ensemble in zero field and a saturating field.

The strong magnetostatic interaction gives rise to groups of energetically bound particles, known as clusters, which exhibit co-operative orientational and spatial migration. These associations are identified using a clustering method which attempts to maximise the configurational entropy and minimise the cluster self energy. The groups of particles so identified are temporarily identified as

a rigid body.

This approach leads to the formation of extended networks consisting of particles in strongly bound clusters which themselves interact and give rise to an extended network. This is similar to the long-range order observed in practical dispersions.

COMPUTER SIMULATION OF SURFACTANT SYSTEMS

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An NVT Monte Carlo simulation of a lattice model of a surfactant and solvent mixture is described. The work is an extension of an earlier model [1] in which surfactant chains are represented as a set of connected hydrophilic and hydrophobic segments lying on a cubic lattice.

In the work presented here, the lattice coordination number has been increased to 26 and chain flexibility is taken into account by associating an energy with each set of two consecutive bonds.

The extensions to the model are computationally demanding and it is necessary to use a more efficient sampling scheme than simple reptation. For this reason, a modification of the configurational bias Monte Carlo (CBMC) scheme is presented. This modification is closely related to the off-lattice system scheme of Frenkel et al. [2]. The efficiency of the new method is compared with standard CBMC [3] and simple reptation.

[1] D. Brindle, and C.M. Care, *J. Chem. Soc. Faraday Trans.*, **88**, 2163 (1992)

[2] D. Frenkel, G.C.A.M. Mooij and B. Smit, *J. Phys. : Cond. Matt.*, **3**, 3053 (1991)

[3] J.I. Siepmann and D. Frenkel *Molec. Phys.*, **75**, 59 (1992)

SIMULATION OF SELF-ORGANISATION AND SELF-ASSEMBLY IN DISCOTIC LIQUIDS

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A model discotic molecule, constructed from a planar hard core of bonded hard spheres and a central square-well attractive site, has been employed in a variety of simulation studies of self-organisation and self-assembly in complex fluids.

Monte Carlo (MC) NpT simulations of a monolayer of these molecules have been used to investigate the competition between standing-up states (condensed liquid) and lying-down states (expanded liquid) in adsorbed monolayers of insoluble disks [1] .

MC NpT simulations of a bulk fluid mixture of these disks and square-well solvent are being used to map out regions of lyotropic liquid crystal behaviour and pre-transitional ordering for a range of volume fractions. The simulations show trends similar to those observed for an analogous experimental system [2]. At lower volume fractions, we are studying the self-assembly of these disks into chain-like aggregates. Results can then be interpreted within the framework of 1-dimensional chemical association theory [3] .

We have also begun initial studies of columnar adsorption onto square-well walls. Such studies of interfacial self-assembly require, in addition, control over the solvent chemical potential.

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THE USE OF CHEMICAL SHIFT MEASUREMENTS TO PROBE THE ONE-DIMENSIONAL SELF ASSEMBLY OF AQUEOUS SOLUTIONS OF THE AMPHIPHILES TP6EO2M AND TP6EO3M

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The discotic amphiphiles TP6EO2M and TP6EO3M self-assemble in water by a simple stacking process. Proton chemical shift measurements in the isotropic phases of these amphiphile / water solutions were seen to be consistent with a thermodynamic model that describes the self-assembly of micelles in concentrated solution. The model was then adapted with a second virial approximation and the excluded volume interactions of the aggregates accounted for up to a volume fraction of 0.1. Thermodynamic parameters of aggregation are obtained as well as the intermolecular separation within the aggregates by modelling the aromatic ring current shift of a TP6EO2M dimer.

Hydration of the hydrophilic ethylene oxy side chains was seen to be an important consideration. Hydration numbers for ethylene oxy / water systems in the literature are dependent on the experimental technique used to obtain them, so careful consideration was required when applying them to these systems. Including the bound water to the side chains in the volume fraction of the aggregates leads to a better fit of the experimental data.

COMPUTER SIMULATION OF HYDROPHOBIC EFFECTS IN ETHANE-WATER SYSTEMS

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Aqueous solutions of nonpolar solutes exhibit several unusual properties called hydrophobic effects. These can be subdivided into two categories. Hydrophobic hydration refers to the microscopic properties of the structure and dynamics of water molecules surrounding a nonpolar solute, and to the thermodynamic properties associated with these dilute solutions. Hydrophobic interaction refers to the solvent-induced forces between two or more nonpolar solute molecules. It is generally believed that these interactions are responsible for several phenomena like the folding and stability of biopolymers and small molecules in solution, the stability of micelles and biological membranes, the aqueous association equilibria of different compounds, and the low solubility of species such as hydrocarbons and the inert gases.

The low solubility of nonpolar molecules in water is thermodynamically characterised by a positive standard Gibbs free energy of dissolution from the gas phase. The enthalpy of solution has been shown to be negative, thus indicating that the nonpolar solute increases the degree of hydrogen bonding of water molecules in the solvation shell so as to maximise the water-water attraction and avoid the solute's hard core, with a substantial unfavourable decrease in the entropy of water. This negative entropy change should be responsible for the observed decrease in the solubility of these solutes with increasing temperature near room temperature, and also for the entropy-driven force that drives such species together. Nonpolar solutes would tend to cluster together to have fewer ordered water molecules surrounding them, with an actual positive entropy change for this process. Since the enthalpy of association should be positive, the extent of hydrophobic aggregation should therefore increase with temperature near room temperature, but there should be a reversal of these trends, as for hydrophobic hydration, at high temperatures, due to the large heat capacity of solution.

This work reports on molecular dynamics simulations carried out on water-ethane mixtures to study the microscopic details of hydrophobic hydration and the extent of aggregation of these solutes in the range 280-350 K. The results on the hydrophobic hydration of a single ethane molecule in water show a temperature-independent structuring of the first hydration shell water molecules, but also an unexpected higher mobility, as revealed by shorter hydrogen-bond lifetimes and a broader distribution of coordination states. The hydrophobic interaction of four ethane molecules in water showed no difference in the tendency of aggregation in the range 280-300 K, but a clear increase in this tendency was observed at 320 K.

WATER STRUCTURE IN AQUEOUS SOLUTIONS OF APOLAR SOLUTES

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Hydrophobic hydration effects are believed to be central to interactions in the aqueous environment involving macromolecular assembly and stability. However, the information on both solute-water and water-water structure at the atomic level in the liquid state is still sparse. We are using a combination of statistical analysis of crystallographic coordinates from protein databases [1], computer simulation [2] and neutron diffraction [3]; to build up a picture of apolar hydration structures. Neutron scattering is currently the best experimental method for getting this information because of the possibility of using H/D substitution difference methods [4]; these provide atomic partial pair correlation functions which can be compared directly with the same functions calculated from computer simulation. The poster presents neutron diffraction and simulation data on water structure around model compounds such as alcohols, tetraalkylammonium (TAA) ions and phenol. The experimental HH and XH correlation functions for the water in alcohol-water mixtures and TAA salt solutions show very little change with increasing “hydrophobicity” of the solute. They support the view that apolar solutes exist in cavities formed in the water but suggest that such cavities have only a small effect in increasing the order in the water.

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DIRECT FREE ENERGY CALCULATIONS FOR CLATHRATE HYDRATES

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In this work we present an extension of the quasi-harmonic method of calculating solid-phase free energies to make it applicable to molecular systems. The method has been used to calcu-

late the phase behaviour of clathrate hydrates, and, in particular, to examine the validity of the assumptions that underlie the semi-empirical formulations that are currently used in engineering applications. Results will be presented for the free energies of various hydrate phases relative to ice, and calculated thermodynamic properties of clathrates as a function of state point. The method is cheap and quick, and makes it possible to contemplate full atomic free energy minimisation calculations on workstations.

COMPUTER SIMULATION OF MODEL FERROELECTRIC PHASES

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Of late, much interest has been shown in ferroelectric mesophases. Ferroelectric chiral smectic- C^* phases provide a molecular framework suitable for the production of a third generation of fast-switching liquid crystalline displays. However, a number of other molecular geometries have been proposed which may lead to useful ferroelectric materials. For instance, it has been proposed that molecules with a component of their molecular dipole parallel to the long molecular axes can form ferroelectric smectic phases (smectic- A_p and smectic- C_p). Such phases rely on over-coming the natural tendency of molecules for anti-parallel dipole ordering, by careful manipulation of intermolecular forces.

In this work we present preliminary results from a Monte Carlo computer simulation study of ferroelectric formation in smectic mesophases. In our model we attempt to manipulate intermolecular forces to favour ferroelectric phases.

LIQUID CRYSTAL ELASTIC CONSTANTS VIA COMPUTER SIMULATION

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A number of recent studies have shown the usefulness of computer simulation as a tool for studying liquid crystal phases [1]. Simulation provides an excellent technique to calculate bulk

liquid crystal properties starting from only a molecular pair-potential. In particular, if molecular dynamics techniques are used, then simulations can yield both static (order parameters and elastic constants) and dynamic properties (diffusion constants) for the bulk fluid phases.

In this paper we present the results of a molecular dynamics simulation study of elastic constants in the nematic phase. The model molecules are based on chains of hard-spheres which are linked together by potential wells. The chains of spheres provide a convenient hard-particle mesogen [2] which can be tuned to allow differing amounts of molecular flexibility. Elastic constants are calculated for two systems with differing degrees of flexibility.

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