SYMPOSIUM P

Multiscale Modeling of Organic Materials

April 24 – 25, 2000

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* Invited paper

SESSION P1: MULTISCALE MODELING
Chairs: Ruth Pachter and Barry L. Farmer
Monday Morning, April 24, 2000
City (Argent)

8:30 AM *P1.1
STATEGIES FOR MULTISCALE MODELING AND SIMULATION OF ORGANIC MATERIALS. W.A. Goddard, III, M. Blanco, T. Cagin, N. Vaidehi, S. Dasgupta, R. Muller, Materials and Process Simulation Center (MSC), Beckman Institute, California Institute of Technology, Pasadena, CA.

Advances in theory and methods are making it practical to consider fully first principles (de novo) predictions of structures, properties, and processes for organic materials. However, despite the progress there remain enormous challenges in bridging the vast range of distances and time scales between de novo atomistic simulations and the quantitative continuum models for the macroscopic systems essential to industrial design and operations. Recent advances relevant to such developments include:
- Quantum Chemistry including continuum solvation and Force Field Embedding (QM/MM)
- De novo Force Fields to describe phase transitions
- Molecular dynamics including continuum solvation
- Nonequilibrium MD for rheology and thermal conductivity
- Mesoscale simulations
To provide some flavor for the opportunities we will illustrate some of the progress and challenges by summarize some recent applications of to industrial problems in catalysis, materials science, and biochemistry that. Topics to be covered will be selected from:
- Structures and Properties of dendritic polymers
- Thermal decomposition and shock decomposition of energetic materials
- Solubility of solutes in polymer systems
- Fullerene tubes
- Melting and Glass Transformations of polymers

9:00 AM *P1.2
MULTIPLE LENGTH AND TIME SCALES IN GLASS-FORMING POLYMERS: NEW INSIGHTS FROM AND CHALLENGES FOR SIMULATION. Sharon C. Glotzer, Polymers Division and Center for Theoretical and Computational Materials Science, National Institute of Standards and Technology, Gaithersburg, MD.

As polymer melts are cooled towards their glass transition, monomers become temporarily trapped in cages formed by their neighbors, and structural relaxation slows dramatically by many orders of magnitude. Recent molecular dynamics simulations of dense, unentangled melts have demonstrated the increased tendency for correlated monomer motion and localization on length and time scales that grow rapidly as the mode coupling temperature T_c is approached from above.[1,2] This dynamical heterogeneity in otherwise structurally homogeneous liquids also occurs in supercooled atomic, molecular and colloidal liquids, and is responsible for the decoupling of diffusion and structural relaxation. It poses a substantial challenge for simulation, since it means that extremely large system sizes, as well as long times, are required to accurately simulate these materials. In this talk we present our recent simulation work on characterizing and quantifying dynamical heterogeneity and the inherent multiple length and time scales that arise in glass-forming polymers and supercooled liquids. We present new results on dynamical heterogeneity and relaxation in filled polymers.[3] Finally, we briefly address the requirements and challenges in constructing acceleration algorithms for modeling glass-forming materials.
[1]C. Bennemann, C. Donati, J. Baschnagel and S.C. Glotzer, Nature 399, 246 (1999); C. Donati, S.C. Glotzer, and P.H. Poole, Phys. Rev. Lett. 82, 5064 (1999); S.C. Glotzer, J. Non-Cryst. Solids, in press, and references therein.
[2]N. Lacevic, T.B. Schroeder and S.C. Glotzer, preprint.
[3]F. Starr, T.B. Schroeder and S.C. Glotzer, in preparation.

9:30 AM *P1.3
PLATFORM FOR MULTISCALE MODELING FOR POLYMERIC MATERIALS. Masao Doi, Department of Computational Science and Engineering, Nagoya University, Chikusa, Nagoya, JAPAN.

A national project has started in Japan last year. It aims at creating software which helps to solve various problems in the development of materials, especially polymeric materials. It has an ultimate target of developing a seamless zooming system which executes virtual experiments for given materials moving around various spatial and time scales. This target is very difficult to achieve, but we believe that CAE for materials needs such technology in future, and we are working to make a prototype for such system. Though the central issue of the problem, how to do multiscale modeling is not completely clarified, we can approach the goal by making tools and libraries which facilitates multiscale modeling. With this view, we are currently (1) developing simulation engines specialized for the meso scale models of polymers (coarse grained molecular dynamics, self-consistent field theory and continuum modeling for material transport), (2) developing a general user interface and (3) validating the software by applying them to real problems. Here I describe our current status and discuss future prospect.

10:30 AM *P1.4
MULTISCALE MODELING OF THE STRUCTURE AND PROCESSING OF LIQUID CRYSTALLINE POLYMERS. Gerhard Goldbeck-Wood, Houjie Tu, Alan H Windle, Univ of Cambridge, Dept of Materials Science and Metallurgy, Cambridge, UNITED KINGDOM.

Structure formation and processing in liquid crystalline polymers (LCPs) involves many different length scales. Key stages are (a) the molecular conformations which are the basis of the tendency to form a liquid crystalline phase, (b) the mesoscale texture of the nematic director field, involving distortion elasticity due to defects as well as interactions with a flow field, and (c) the relation of the mesoscale dynamics with the macroscopic rheology during processing, and the final part structure. This paper outlines computer modelling of these different stages, as well as approaches towards linking them. The molecular modelling stage involves generating ensembles of single chains in order to calculate the persistence length. We compare force field and ab initio based simulations. The molecular data are used to parameterize the mesoscale modelling: Frank elastic constants, rotational diffusion constant and Ericksen shape parameter are determined. On the mesoscale, we represent the textured director field on a cubic lattice with nearest neighbour interactions. Our dynamics algorithm includes the flow response as formulated by the Ericksen equation and the distortion elastic response based on three independent Frank constants. The simulations highlight the non-linearity of defect-flow interactions, and show that the tumbling tendency as well as the relatively low twist elastic constant of LCPs tends to lead to domains aligned in the 'log-rolling' direction, hence be a source of defects. Stress calculations show a shear thinning behaviour. On the processing level we are addressing the structure formed during injection molding by linking up the mesoscale model with mold filling software. Our focus is the case of two flow fronts meeting and forming a weldline which to date is said to be the most important weakness of LCPs in applications.

11:00 AM *P1.5
LARGE SCALE MOLECULAR DYNAMICS SIMULATIONS OF A 4-N-PENTYL-4′-CYANOBIPHENYL LIQUID CRYSTALLINE MODEL: BULK AND SURFACE PROPERTIES. Zhiqiang Wang, James A. Lupo, Soumya S. Patnaik and Ruth Pachter, Air Force Research Laboratory, Materials & Manufacturing Directorate, AFRL/MLPJ, Wright-Patterson AFB, OH.

Molecular dynamics simulations of a 4-n-pentyl-4′-cyanobiphenyl (5CB) liquid crystalline model in the bulk and regarding the surface, with as many as 944 5CB molecules (35872 atoms), were carried out utilizing scalable high performance computing capabilities and a new implementation of the fast multipole method to treat long-range interactions efficiently. For the droplet, unlike previous works on much smaller systems, the correlation between droplet shape and the nematic order director could be elucidated.Orientational order parameters, phase transitions at different temperatures, also including surface constraints, will be presented. The effects of the computational cell size on the calculated results will also be discussed.

11:30 AM P1.6
MOLECULAR DYNAMICS CALCULATION TO CLARIFY THE RELATIONSHIP BETWEEN STRUCTURE AND MECHANICAL PROPERTIES OF POLYMER CRYSTALS. Kohji Tashiro, Department of Macromolecular Science, Osaka University, Osaka, JAPAN.

Molecular dynamics (MD) calculation was made in order to clarify the relationship between structure and mechanical properties of polymer crystals such as polyoxymethylene and polyethylene. Before the MD calculations, the potential functions were refined so that the X-ray analysed lattice parameters and vibrational spectroscopic data were reproduced as reasonably as possible. The MD calculations were made under the NPT conditions at the various temperatures for the crystal structure models consisting of several thousands of atoms under the periodic boundary conditions. The temperature dependence of the Young's modulus along the chain axis was calculated. The large decrease of the modulus was related with the conformational disordering at higher temperature. In the case of orthorhombic polyethylene, the rotational and translational motions of the molecular chains were found to occur progressively above room temperature, being reasonably related with the remarkable changes in

the crystal structure revealed by the X-ray analysis as well as the temperature dependence of the Young's modulus.

11:45 AM P1.7
TIME AND TEMPERATURE DEPENDENCE OF THE LINEAR AND NONLINEAR OPTICAL PROPERTIES OF NEMATIC LIQUID CRYSTALS. Kim F. Ferris and Gregory J. Exarhos, Pacific Northwest National Laboratories, Richland, WA; Steven M. Risser, Battelle Memorial Institute, Columbus, OH.

Although it is now relatively simple to calculate the optical properties of single molecules, the anisotropy of the molecules, their partial ordering, and the dynamical fluctuations of the molecules hinder description of the macroscopic optical properties of liquid crystals. In recent work, we have begun development of methods to calculate the macroscopic optical properties of nematic liquid crystals, starting from the optical properties of the individual nematogens. In this work, we continue this development, focusing on the variation of the optical properties with time and temperature. In this paper, we perform molecular dynamics simulations of liquid crystals using periodic boundary conditions and a reparameterized version of the MM3 force field. We then perform electronic structure calculations on the individual nematogens, using the previously developed methods, to calculate the macroscopic nonlinear optical properties of the system. By performing these calculations during the course of the MD simulation, we can examine the relation between fluctuations in the optical properties of individual molecules and those of the macroscopic system. By altering the temperature of the MD simulation, we can also examine how the macroscopic optical properties are tied to both the order parameter and geometrical fluctuations of individual molecules. This work was supported in part by the US Department of Energy, Office of Science, Materials Sciences Directorate under contract DE-AC06 76 RLO 1830.

SESSION P2: MATERIALS MODELING
Chairs: Barry L. Farmer and Kohji Tashiro
Monday Afternoon, April 24, 2000
City (Argent)

1:30 PM *P2.1
MODELING SILICON SURFACES AND SILICON-BASED MATERIALS. Mark Gordon, Iowa State University, Ames, IA; Takako Kudo, Gunma University, Kiryu, JAPAN; James Shoemaker and Larry W. Burggraf, Air Force Institute of Technology, WPAFB, OH.

The first part of this talk will discuss the use of ab initio quantum chemistry to elucidate the mechanism of formation of polyhedral oligomeric silsesquioxanes (POSS), including the impact of the presence of solvent molecules. The seond part will begin with an introduction to the new surface chemistry method SIMOMM (Surface Integrated Molecular Orbital Molecular Mechanics). This will be followed by applications of the method to interesting reactions.

2:00 PM *P2.2
THEORETICAL SYNTHESIS OF RANDOM POLYMERS BASED ON THE MO METHOD AND ITS APPLICATIONS TO POLYPEPTIDES AND POLYSILANE DERIVATIVES. Yuriko Aoki, Hiroshima Univ, Dept of Chemistry, Higashi-Hiroshima, JAPAN.

A new quantum chemical method was developed toward the theoretical synthesis for aperiodic polymers like conducting polymers and polypeptides. In this method, the canonical wave function of a so called starting cluster is localized, the interaction between this cluster and an attacking monomer included, followed by the localization of the new wavefunctions and so on. This treatment enables us to obtain the electronic states of large clusters, treating only a few units at a time of the total system. This treatment is already developed at the levels of various semi-empirical and ab initio molecular orbital methods. In this treatment, the interactions between the localized molecular orbitals (LMOs) of a cluster and the canonical molecular orbitals of an attacking monomer are successively included by solving the Hartree-Fock equation. The LMOs as well as the atomic orbitals, which are unaffected from the attacking monomer, are always removed so that the two-electron integrals made during the cluster elongation are greatly reduced. The reliability and the efficiency of this method are examined via applications to polyethylene, polyacetylene, and polypeptides. It was shown that the present method saves significantly the computational time in large cluster calculations, and provides good agreements with the results by the conventional direct treatment for the whole system. Furthermore, this treatment was developed for the stratified synthesis of the electronic states between oligomers using parallel computers. By this treatment, a simultaneous synthesis of electronic states for huge peptides becomes feasible. This method was applied for the elucidation of cooperative phenomenon in the conformation of polysilane derivatives. It may be expected that these methods are adequately applicable to large aperiodic polymers with a great advantage in computational time and very efficient for functional designs in various polymer systems.

2:30 PM *P2.3
COUNTER ION EFFECTS IN ORGANIC ELECTRONIC AND PHOTONIC MATERIALS. Douglas S. Dudis, A. Todd Yeates, Guru P. Das and Xiaofeng Duan, Air Force Research Laboratory, Materials and Manufacturing Directorate, Wright-Patterson APB, OH.

Most organic molecules and polymers of interest for electronic and photonic applications are highly conjugated. Extensive electron delocalization dominates these materials in the pristine and doped forms. Many interesting properties are found in the doped form, in which doping entails chemical oxidation or reduction of the organic moiety. Most modeling of these materials occurs in vacuo, that is, in the absence of any counter ion. Such counter ions are always present in physical samples, their presence being required for charge balance. But more than balancing the charge, the dopant can dramatically influence the overall material properties. For example, in polythiophene, the choice and extent of dopant can dictate whether polarons or bipolarons are formed. Polarons are paramagnetic while bipolarons are diamagnetic, so the magnetic properties are very much influenced by counter ions. In this present work we will present modeling approaches to understand simple doping processes in conducting organic materials as well as counter ion influences on third order nonlinear optical responses.

3:30 PM *P2.4
SPECTROSCOPICALLY DETERMINED FORCE FIELDS: A ROUTE TO MORE ACCURATE POTENTIAL ENERGY FUNCTIONS. Samuel Krimm, Dept of Physics, Univ of Michigan, Ann Arbor, MI.

The quantitatively reliable prediction of structural and dynamical properties of organic materials (such as polymer molecules) depends on the ability of molecular mechanics (MM) energy functions to accurately reproduce a large range of molecular properties. Most current MM functions give good prediction of conformational structures and energies, but they are inadequate in reproducing spectroscopically acceptable vibrational frequencies. However, the accurate prediction of this property is probably the most sensitive test of the reliablity of the form and parameterization of the MM function. To achieve such predictability, we have developed a method that incorporates frequency agreement together with energy and structure reproduction in the initial parameterization of the force field. The method is based on an analytic transformation of ab initio structures and experimentally scaled force fields into the format of an MM function [1]. We call such a force field a Spectroscopically Determined Force Field (SDFF). The use of ab initio calculations as the basis for the parameterization provides important additional data to test the force field. The procedure has been implemented to produce SDFFs for alkane [2,3] and alkene [4] chains that give frequency agreement to within rms deviations of 5-10 cm^{-1}. These force fields have been applied to predictions of the chain arrangement in crystalline syndiotactic polypropylene [5] and to the chain modulus of crystalline polyethylene [6], the latter being reproduced to within about 1% of the experimental value. 1.K. Palmo, L.-O. Pietila, S. Krimm, J. Comput. Chem. 12 (1991) 385. 2.K. Palmo, N.G. Mirkin, L.-O. Pietila, S. Krimm, Macromolecules 26 (1993) 6831. 3.K. Palmo, N.G. Mirkin, S. Krimm, J. Phys. Chem. A 102 (1998) 6448. 4.B. Mannfors, T. Sundius, K. Palmo, L.-O. Pietila, S. Krimm, J. Mol. Struct., in press. 5.K. Palmo, S. Krimm, Macromolecules 29 (1996) 8549. 6.K. Palmo, S. Krimm, J. Polymer Sci.: Part B: Polymer Physics 34 (1996) 37.

4:00 PM P2.5
UREA: AN AB-INITIO AND FORCEFIELD STUDY OF THE GASEOUS AND SOLID PHASES. Huai Sun*, Paul W.-C. Kung, Molecular Simulations Inc., San Diego, CA. *Present address: Alanex Corp., San Diego, CA.

We have studied the gaseous and solid phases of urea using both density functional theory (DFT) calculations and forcefield simulations. Based on the understanding gained from these DFT calculations, we have derived class II forcefield parameters appropriate for urea in the two phases. The solid phase parameters were then used in molecular dynamics simulations and shown to agree with the experimental solid phase densities of urea to better than 2% in the temperature range from 12 to 293K.

4:15 PM *P2.6
CONFORMATIONAL CHARACTERISTICS OF POLY (METHYLENE SULFIDE), POLY (ETHYLENE SULFIDE), AND POLY(PROPYLENE SULFIDE). Yuji Sasanuma, Nobuyuki Miura, Misa Sawanobori, Hajime Ohta and Yugo Hayashi, Chiba Univ, Dept of Materials Technology, Chiba, JAPAN; Akira Kaito, NIMC, Dept of Polymer Physics, Tsukuba, JAPAN.

Conformational characteristics of poly(methylene sulfide) ($[\text{-}CH_2\text{-}S\text{-}]_n$, PMS), poly(ethylene sulfide) ($[\text{-}CH_2\text{-}CH_2\text{-}S\text{-}]_n$, PES), and poly(propylene sulfide) ($[\text{-}CH_2\text{-}CH(CH_3)\text{-}S\text{-}]_n$, PPS) have been investigated by a combined use of experimental and theoretical techniques. The bond conformations of the C-S and C-C bonds of the monomeric model compounds were determined by analyzing NMR vicinal carbon-proton and proton-proton coupling constants, respectively. The conformational free energies of the model compounds were evaluated from the ab initio molecular orbital calculations at the MP2/6-311++G(2d,p)//MP2/6-311++G(d,p) level, and broken down into some conformational energies. For all the compounds, the experimental bond conformations were satisfactorily reproduced from the conformational energies. From the above analysis, the conformational characteristics of the unperturbed polysulfides were revealed as follows. The C-S bond of PMS has a strong *gauche* preference, as found for poly(methylene oxide). For PES and PPS, the C-C bonds prefer the *trans* conformation, while the C-S bonds prefer the *gauche* state. In contrast to poly(ethylene oxide) and poly(propylene oxide), whose C-C bonds exhibit the *gauche* preference due to the attractive (C-H)$\cdots$O interactions, PES and PPS were shown not to form any attractive intramolecular (C-H)$\cdots$S interactions.

4:45 PM P2.7
COMBINING DENSITY FUNCTIONAL THEORY AND SELF-CONSISTENT FIELD MODEL TO STUDY PHASE BEHAVIOR OF POLYMER/INORGANIC MIXTURES.
Valeriy V. Ginzburg and Anna C. Balazs, Dept of Chemical and Petroleum Engineering, University of Pittsburgh, Pittsburgh, PA.

We combine a density functional theory (DFT) with a self-consistent field model (SCF) to calculate the phase behavior of thin, oblate colloidal particles that are coated with surfactants and immersed in a polymer melt. The perturbation-theory DFT is used to describe the macroscopic positional and orientational ordering of nanoparticles. The entropic and enthalpic free energy of surfactant molecules and their interactions with the surrounding polymer chains is modeled using the Scheutjens-Fleer SCF theory. The resulting free energy profiles are then used as an input for the DFT calculations. We calculate phase diagram for several model systems and compare them with known experimental results for polymer/clay nanocomposites.

SESSION P3: MESOSCALE MODELING
Chairs: Soumya S. Patnaik and David Rigby
Tuesday Morning, April 25, 2000
City (Argent)

8:30 AM *P3.1
FUNCTIONAL MODELS FOR CONTROLLED POLYMER VESICLE FORMATION. J.G.E.M. Fraaije, University of Leiden, THE NETHERLANDS.

A variety of simulation methods for 3D pattern formation in complex amphiphilic systems have been developed over the last few years: molecular dynamics with simplified forcefields, dynamical Monte Carlo, lattice Boltzmann techniques, cell dynamical methods, and dynamic density functional methods. In all these methods the focus is on the supra-molecular or mesoscopic level. In this paper we discuss the application of the dynamic density functional method to the self-assembly of block polyelectrolyte molecules into robust polymer vesicles. The building blocks consist of sequences of dissimilar monomers, connected in copolymer chain molecules. Factors such as the composition and architecture of the polymers control the self-organization phenomena. The results are presented as snapshots of 3D morphology development of quenched copolymer 'nano' droplets (size 100-1000 nm): from droplets, to vesicles, to leaky vesicles, to cages, to worms. We propose that by careful selection of mixing pathway and solvent, new types of porous polymer vesicles can be made. In the end, the goal is the invention of methods for the rational design of truly complex polymer vesicles, with multiple compartments, and controlled porous morphologies.

9:00 AM P3.2
A MESOSCALE LATTICE CHAIN MODEL OF BULK POLYMERS: STRUCTURE AND DYNAMICS AT INTERFACES, CRYSTALLIZATION, AND BLOCK-COPOLYMERS AND SURFACE STRUCTURE. Gerhard Goldbeck-Wood, Kelly Anderson, Tim Carver, Michael Kyle, Alan Windle, Univ of Cambridge, Dept of Materials Science and Metallurgy, Cambridge, UNITED KINGDOM; Jiandong Ding, Fudan University, Dept of Macromolecular Science, Shanghai, CHINA.

Coarse grained chain models have proved to be very powerful in aiding our understanding of the structure and properties of polymers. In our mesoscale polymer model chains are represented by a connected path of nearest neighbour lattice points on a face centred cubic lattice. The model hence benefits from a high coordination number while retaining the numerical efficiency of lattice models. Chain movement arises through exchange of a vacancy with a site occupied by a polymer segment, according to a kinetic Monte Carlo algorithm with explicit rules of allowed movement. Static as well as dynamic scaling laws, including the crossover from Rouse to reptation dynamics, are well reproduced. Results of several applications of the model will be presented. In polymer welding simulations we find molecular interpretations of Wool's empirical relationships. Polymer crystallization is modelled by introducing a favourable interchain interaction energy associated with neighbouring bonds that are oriented parallel to each other. The model therefore inherently simulates the competition between the entropy of the chains and the enthalpy of chain alignment. We simulate the chain folding of individual chains into either a single or multiple nuclei depending on chain length, and the formation of growth layers onto a crystal surface, with a kinetically determined fold length. An extension of the model to diblock-copolymers shows the typical microphase separated structures. The orientational order, chain stretching and shape of the chains have been studied. The surface structure of polymer-air and polymer-substrate interfaces have been studied and their roughness analysed as a function of chain length and interaction parameters.

9:15 AM P3.3
MESOSCALE MODELING STUDY OF NEMATIC LIQUID CRYSTALS CONFINED TO ELLIPSOIDAL DOMAINS.
Rishikesh K. Bharadwaj, Systran Federal Corporation, Dayton, OH; T.J. Bunning, B.L. Farmer, Air Force Research Laboratory, Materials and Manufacturing Directorate, WPAFB, OH.

Director configurations of nematic liquid crystalline molecules packed in ellipsoidal domains have been investigated using mesoscale modeling techniques. Interactions between the directors were described by the Lebwohl-Lasher potential. Four different ellipsoidal shapes (sphere, oblate spheroid, prolate spheroid, and ellipsoid) were studied under homogeneous and homeotropic surface anchoring conditions. The model has been characterized by computing thermodynamic and structural properties as a function of ellipsoidal shape (prolate and oblate) and size. The predicted director configuration in ellipsoids resulting from homeotropic surface anchoring is found to be very different compared to that in spherical domains. The bipolar configuration involving homogeneous surface anchoring is nearly identical in the four cases. The effect of an external electric field applied at different orientations with respect to the major axis of the ellipsoid has been probed as a function of the magnitude of the field and ellipsoidal size and shape. The orientation of directors is most easily accomplished parallel and perpendicular to the major axis for the oblate and prolate spheroids respectively for homeotropic anchoring and along the bipolar symmetry axis for homogeneous anchoring. In domains with homeotropic surface anchoring, the oblate spheroid and elongated ellipsoid, and for homogeneous anchoring conditions, the prolate spheroid and elongated ellipsoid are predicted to be the most efficient geometries for PDLC applications.

9:30 AM P3.4
COLLABORATIVE OPERATION OF MOLECULAR DYNAMICS SIMULATION AND MEAN FIELD CALCULATION. Takeshi Aoyagi, JCII, Nagoya, JAPAN; Jun-ichi Takimoto, Yamagata Univ, Dept of Materials Science and Engineering, Yonezawa, JAPAN; Masao Doi, Nagoya Univ, Dept of Computational Science and Engineering, Nagoya, JAPAN.

An example of collaborative operation of molecular dynamics (MD) simulation and mean field calculation is performed to predict mesoscale morphology and mechanical properties of various polymeric systems. We developed an efficient algorism to construct an equilibrated configuration of polymer chains by combining MD simulation with mean field calculation. A biased potential is applied to accelerate molecular dynamics to reach the equilibrated state. The biased potential is determined from the target density distribution, which is obtained by mean field calculation. The chain configuration, which has the consistent density distribution with the results of mean field calculation, is obtained in relatively short MD simulation using this algorism. Some enhanced methods to build an initial configuration of polymer chains using the results of mean field calculation are also studied. The new algorism is applied to predict micro domain structure and chain configuration of thermal plastic elastomer. The chain configuration is created efficiently and the elastic behavior of pseudo network structure is reproduced by coarse-grained molecular dynamics simulation.

9:45 AM *P3.5
MULTISCALE MODELING OF DENSE POLYMER SYSTEMS.
Kurt Kremer, Max-Planck-Institute for Polymer Research, Mainz, GERMANY.

At a first sight it is tempting to simulate a melt of polymers on the atomistic level. Such a simulation should then provide complete information about the properties of the system. It is almost trivial to show that even with the present high speed computers such a simulation is impossible. On the other hand, it is questionable whether such an attempt should be undertaken at all. It would provide data containing a huge amount of irrelevant information. As it holds for all disordered complex macromolecular materials polymers can be characterized by a hierarchy of different length and time scales. Especially time scales span an extremely wide range. On the microscopic level dynamics is dominated by the local oscillations of bond angles. On the semi-macroscopic level the behavior is dominated by the overall diffusion of the chains or the relaxation of the overall conformation of the objects. These times depend on chain length and temperature can easily span more than 10 decades. In this sense I will discuss first attempts to bridge the gap from microscopic to mesoscopic and thereafter to the semi-macroscopic regime within a simulation scheme. I will describe a mapping procedure to go from microscopic to a mesoscopic description. Thereafter, first steps toward the next level of description are discussed. Starting from the conformations of polymer chains on the coarse grained level, the chains are mapped onto an extended soft particle with only three internal degrees of freedom compared to the 0 (3N) degrees of freedom of the whole object. References: W. Tschop et al, Acta Polymer., Vol. 49, 61, 75 (1998) J. Eilhard et al, J. Chem. Phys., Vol. 110, 1819 (1999) M. Murat and K. Kremer, J. Chem. Phys., Vol. 108, 4340 (1998).

10:30 AM *P3.6
ACCURATE MODELS FOR HYDROCARBONS ON COARSE GRAINED LATTICE. Ananth Indrakanthi, Sanat Kumar, Pennsylvania State University, University Park, PA; Athanassios Panagiotopoulos, Dept. of Chemical Engineering, University of Maryland, College Park, MD.

In past work we have examined the phase behavior of lattice restricted primitive models for integer values of the ratio of ionic diameter to lattice spacing, ξ. For $\xi \leq 2$ there is coexistence between a disordered phase and an antiferromagnetic phase, but no vapor-liquid equilibrium. For $\xi \geq 3$, a region of normal vapor-liquid coexistence is found, with critical temperatures and densities which arevery close to their continuous space counterparts. Our findings stress the important philosophical point that lattice structure can result in qualitatively different physics from continuous space models, but that the two models converge even for relatively coarsely discretized lattices. This provides us with a simple means of constructing mesoscale models for hydrocarbon based polymers, where we shall use coarse grained lattice descriptions to accurately potray the properties of these materials, but at a fraction of the cost of an off-lattice calculation. This simplification also permits for the simulations of blend phase behavior in these systems, where truly long chains have to be modeled.

11:00 AM *P3.7
SMALL AND LARGE SCALE STRUCTURE OF RANDOM NETWORKS. B.E. Eichinger, Molecular Simulations Inc., San Diego, CA; Peter Sher, Sines and Symbols, Poway, CA.

Random networks are formed in the crosslinking or cure of polymers. The structure of these materials is imperfect, with local defects (loops, dangling ends, and multiple bonds) arising from variations in the local opportunities for bonding to neighbors. At longer length scales, statistical fluctuations in the topology (pattern of interconnections within arbitrarily large collections of molecules) provide another source of inhomogeneity. These phenomena are being explored with an off-lattice percolation algorithm that mimics kinetically controlled cure chemistry. The results of validation tests will be compared with experiments, and applications to several different types of cure chemistry will be described.

11:30 AM P3.8
COARSE GRAIN DYNAMICS SIMULATIONS OF DENDRIMERS. Tahir Cagin, Materials and Process Simulation Center and Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA.

Dendrimers and hyperbranched polymers represent a novel class of structurally controlled macromolecules derived from a branches-upon-branches structural motif. The synthetic procedures developed for dendrimer preparation permit nearly complete control over the critical molecular design parameters, such as size, shape, surface/interior chemistry, flexibility, and topology. Dendrimers are well defined, highly branched macromolecules that radiate from a central core and are synthesized through a stepwise, repetitive reaction sequence that guarantees complete shells for each generation, leading to polymers that are monodisperse. This property of dendrimers makes it particularly natural to coarsen interactions in order to simulate dynamic processes occuring at larger length and longer time scales. The coarse grain interaction parameters are obtained from atomic interaction parameters to represent the interaction between supramolecular assemblies. The self assembly problem of globular dendritic molecules such as PAMAM can be reduced to a limited number of center-center interactions between them rather than millions of interactions between the individual atoms of a PAMAM dendrimers. We will demonstrate the use of the coarse grained force fields derived by this method in a bulk phase molecular dynamics simulation of generation-7 PAMAM dendrimers in periodic boundary conditions. Furthermore, this approach by eliminating the high frequency modes leads orders of magnitude larger simulation times.

11:45 AM P3.9
MODELING GROWTH OF HARD SEGMENT DOMAINS IN A THERMOPLASTIC URETHANE ELASTOMER. R.V. Browning, S.G. Bardenhagen, E.B. Orler, D.A. Wrobleski, D.K. Graff, Los Alamos National Laboratory, Los Alamos, NM.

Many thermoplastic urethanes (TPUs) are made of blocks of different monomers that prefer to separate, but are linked so that complete segregation is frustrated. For example, soft segments of poly(butylene adipate) can be attached to hard segments made from butanediol and diphenylmethane-4,4′-diisocyanate. At high temperatures the hard and soft segments are well mixed. However, if a sample is suddenly quenched to a lower temperature, then phase segregation can take place and at the same time weak crosslinking can occur via hydrogen bonds. At the macroscopic level there are major changes in the apparent mechanical and thermal characteristics that occur over time intervals of hours to years. Interestingly, related time dependent changes are observed spectroscopically at wavenumbers related to hydrogen bonding. We present results of spectroscopic, DMA and DSC tests to demonstrate this for a specific TPU material. To model this behavior we propose using a combination of a traditional Prony series representation modified to treat temperature dependence coupled with a hard segment domain growth model related to the Avrami equation. Obtaining reasonable behavior over a wide range of temperatures is a major goal of this model. The Prony series coefficients are specified as functions of temperature so that the general behavior observed in a dynamic mechanical analysis test can be reproduced. The time and temperature dependence of the growth of hard segment domains is modeled by using some concepts from Avrami, but we develop instead a state variable differential equation. This equation is calibrated against mechanical tests, but also predicts the time dependent behavior of spectroscopic measurements related to the hydrogen bonding density. We also try to interpret the model coefficients in terms of fundamental characteristics of the polymer system, such as self diffusion rates and hydrogen bonding strengths.

SESSION P4: COMPLEX FLUIDS
Chairs: Ruth Pachter and Soumya S. Patnaik
Tuesday Afternoon, April 25, 2000
City (Argent)

1:30 PM *P4.1
MESOSCALE MODELLING OF COMPLEX FLUID HYDRODYNAMICS. Julia Yeomans, University of Oxford, Department of Physics, Oxford, UNITED KINGDOM.

The hydrodynamics of complex fluids can be complicated and very different from that of simple liquids because of the coupling between the microscopic structure and the velocity fields imposed by the flow. Examples are changes in viscosity under shear, shear banding, or the appearance of Williams domains in liquid crystals subject to an electric field. Modelling these phenomena is difficult because of the interplay between microscopic and macroscopic physics. In an attempt to investigate such flows recent years have seen the development of mesoscale modelling methods which solve the hydrodynamic equations of motion whilst inputting sufficient, albeit approximate, information to model the important microscopic physics of a given fluid. I shall discuss some recent progress in this area. One example will be lattice Boltzmann simulations of dilute polymer solutions and liquid crystals. A second will discuss coupling molecular dynamics simulations of polymer molecules to a hydrodynamic bath modelled using a stochastic algorithm developed by Malevanets and Kapral.

2:00 PM P4.2
MODELLING RIGID-ROD SUPSENSIONS IN HYDRODYNAMIC FLOWS. Colin Denniston, Theoretical Physics, Oxford, UNITED KINGDOM; Enzo Orlandini, Dept of Physics, INFN, Padua, ITALY; Julia Yeomans, Theoretical Physics, Oxford, UNITED KINGDOM.

We will present a lattice Boltzmann algorithm to simulate the dynamics of rigid-rod suspensions, such as liquid crystals, which includes hydrodynamics. To illustrate the scheme, we will show simulations of phase separation under simple flow conditions, such as

shear banding, as well as more complicated oscillatory patterns such as the mechanical analogue of Williams domains in liquid crystals. We will also show how the phase ordering dynamics, after a quench to an ordered phase from a less ordered phase, depends on where you quench to in the non-equilibrium phase diagram.

2:15 PM *P4.3
MULTISCALE MODELING OF COMPLEX FLOWS OF POLYMER SOLUTIONS. Richard Jendrejack, Michael Graham and Juan J. de Pablo, University of Wisconsin, Department of Chemical Engineering.

A hybrid continuum/molecular method is employed to study the rheological properties of polymer solutions in complex geometries. In the spirit of the CONNFFESSIT approach (Calculation of Non-Newtonian Flows; Finite Element Stochastic Simulation Technique), velocity profiles are determined from continuum conservation equations (momentum balance); the stresses required by those equations are determined directly from molecular simulations. Note, however, that in this work a spectral method is employed to solve the continuum equations, as opposed to a finite-element technique. In this talk results will be presented for two systems: a concentrated suspension of rigid fibers, and a dilute solution of long polymer molecules. The latter molecules are modeled as a collection of interaction sites connected by flexible springs. Interactions between sites include excluded volume effects and, for the first time, fluctuating hydrodynamic effects.

2:45 PM P4.4
EFFECTS OF POLYMER-SURFACE INTERACTIONS ON THE RHEOLOGY OF CONFINED ALKANES. Rajesh Khare and David Rigby, Molecular Simulations, Inc., San Diego, CA.

Rheological and structural properties of polymers play a very important role in many industrial applications such as polymer processing and lubrication. The most commonly employed boundary condition in continuum mechanics treatments of these processes - that of stick or no-slip at the interface between fluid and confining surface - has been called into question by recent experimental evidence. These slip effects are believed to give rise to problems such as surface roughness of finished products in polymer processing operations. One of the critical factors affecting wall slip is the nature of the fluid-surface interactions. With this motivation, we have used molecular dynamics simulations to investigate the shear flow behavior of alkanes and alcohols confined between a variety of surfaces. We use atomistically-detailed models for both the sheared fluid and the confining surfaces, with interactions described using the COMPASS force field. The confined fluid consists of linear and branched alkanes and hydroxyl-terminated linear chains. Three different types of confining surfaces are investigated: (1) Pure metal surfaces (2) metal oxide surfaces, and, (3) surfaces carrying grafted chains. The interactions between the sheared fluid and the confining surfaces vary widely among these different types of surfaces, and indeed, these different interactions are shown to lead to strikingly different rheological behavior for the sheared fluid. Thus, on one hand, alkanes confined between pure metal surface (iron) are shown to exhibit no-slip boundary conditions, while alkanes confined between metal oxide (iron oxide) surfaces are shown to exhibit slip at the interface between the sheared fluid and the confining walls. In all cases, flow behavior (e.g. velocity and temperature profiles) of the confined fluid is shown to be consistent with the continuum mechanics predictions for these properties.

3:00 PM P4.5
SPINODAL DECOMPOSITION OF HYDRODYNAMIC BINARY FLUID WITH PARTICLES. Feng Qiu, Gongwen Peng, Valeriy V. Ginzburg, Anna Balazs, Univ of Pittsburgh, Dept of Chemical Engineering, Pittsburgh, PA; Hsuan-Yi Chen, David Jasnow, Univ of Pittsburgh, Dept of Physics and Astronomy, Pittsburgh, PA.

We studied the phase dynamics of a binary fluid containing particles by computer simulation in two dimensions. A time-dependent Ginzburgh-Landau equation coupled with a Navier-Stokes equation to solve the hydrodynamic interactions is numerically integrated in the calculation. Into the fluid mixture, we introduce immobile particles that have coupling interactions with one component of the fluid. We found that hydrodynamic effects are only important in the intermediate stage of domain growth. At later stage, the domain growth slows down and finally is pinned at some finite size. The pinning size of the domains decreases with the increase of the number density of particles and the coupling strength between particles and fluid.

3:30 PM *P4.6
MESOSCALE PATTERNS FROM A DOI-MARRUCCI-GRECO MODEL FOR LIQUID CRYSTAL POLYMERS. M. Gregory Forest, Dept of Mathematics, Univ of North Carolina, Chapel Hill, NC; Qi Wang, Dept of Mathematical Sciences, I.U.P.U.I., Indianapolis, IN; Hong Zhou, Dept of Mathematics, Univ of California, Santa Cruz, CA.

We are interested in micron-scale patterns and textures that form in liquid crystal polymers during and after cessation of shear and elongational flow. The Doi-Marrucci-Greco moment-averaged continuum model is applied to construct exact solutions that pose as analytical models for experimental observations of bands and core defects. We focus on the structure of the tensor model equations, and special heterogeneous solutions which exist in the balance between excluded-volume and distortional elasticity potentials, both with and without an imposed shear or elongational flow. We exhibit light scattering intensity patterns inferred from the banded structures, and geometrical orientation patterns associated with the core defect solutions.

4:00 PM *P4.7
Abstract Withdrawn

4:30 PM P4.8
MODELING MECHANICAL RESPONSE IN NACRE BASED ON ORGANIC-INORGANIC INTERFACIAL PROPERTIES USING 3D FINITE ELEMENT ANALYSIS. Dinesh Katti, Kalpana Katti, Department of Civil Engineering, North Dakota State University, Fargo, ND.

Nacre, the inner layer of seashells is a ceramic laminated biocomposite with exceptional mechanical properties of fracture toughness and strength. The organic layers in the composite play a significant role in the mechanical response of nacre to stresses. In this work, three dimensional finite element models of nacre (constructed in our previous work to design brick and mortar micro-architecture of nacre) were used to study influence of nonlinear response of organic component. In our previous work, the macro response of nacre is modeled using elastic models under low stresses. This work represents stage II of our efforts to model macro response of nacre based on micro scale material parameters. In this work, nonlinear elasto-plastic models for organic component are applied to model the mechanical response of nacre. The influence of the organic layer, inorganic component and the organic-inorganic interfaces is quantitatively evaluated. Using the reported macro response of nacre, elasto-plastic models for organic component are applied to accurately simulate the response at organic-inorganic interfaces.

4:45 PM P4.9
DYNAMIC DENSITY FUNCTIONAL STUDY OF PHASE SEPARATED STRUCTURES OF THIN POLYMER BLEND FILMS. Hiroshi Morita, Japan Chemical Innovation Inst, JAPAN; Toshihiro Kawakatsu, Masao Doi, Department of Computational Science and Engineering, Nagoya University, JAPAN.

We investigate the phase separated structure at free surface of thin polymer blend films using dynamic density functional simulations. Experimental results of Kajiyama's and some other groups show the surface roughening of thin polymer film. We assume that the surface roughening structure induced by phase separation is modeled as the droplet phase on the other layered phase. Under this assumption, we consider the equilibrium of surface tension among two polymer phases and air phase, and we can decide the conditions for the droplet structure at free surface. Furthermore, we succeed in constructing the phase diagram of surface roughening conditions using this equilibrium. From these conditions, we can represent these structures from our simulations. Our results confirm the experimental results, which are reported previously.