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COMPUTATIONAL METHODS FOR POLYMERS AND LIQUID CRYSTALLINE POLYMERS

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Directors of the Workshop: P. Pasini, S. Žumer

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Polymer-Mediated Adhesion.
A Statistical Approach

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The statistical behavior of linear chains confined in a thin slab is investigated theoretically as a model of polymer-mediated adhesion. We apply transition-matrix methods to two lattice models of the polymer: model A consists of end-grafted monodisperse polymer chains, model B of randomly grafted, infinitely long chains.

We evaluate both the elongational and the tangential moduli, the first being generally larger than the latter. By a Flory-Huggins approach we also derive the contribution to the elongational modulus of the polymer compressibility.

Polymer Internal Viscosity.
Friction Against a Hard Surface

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Polymer internal viscosity arises from energy loss through the rotational energy barriers, according to Eyring's model.

The theory explains several aspects of polymer dynamics on the local scale, such as the high-frequency complex modulus of polystyrene in Aroclor solvents and the dynamic structure factor of polyisobutylene as compared with PDMS (Richter et al., 2001).

The theory is applied to the problem of polymer friction against a hard surface; it is shown that the effective friction coefficient varies with the relative velocity V as $V^{-1/2}$ and as V^{-2}, depending whether V is smaller or larger than a critical limit, in qualitative agreement with recent experimental observations by Israelachvili et al.

Mesoscopic modelling of polymers and liquid crystals

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Dynamic processes in synthetic and biopolymers extend over a very wide range of length and time scales and this presents a particular challenge to computer simulation. Exciting advances in polymer simulation methodology however are now providing access to an increasingly wide range of phenomena.

Whilst atomistic level molecular dynamics (MD) simulations can be used to probe the dynamics of segmental motion in pure homopolymers, new mesoscopic 'coarse grain' simulation techniques such as dissipative particle dynamics (DPD) operate on structurally a much less detailed scale and give access to the dynamics of polymer solutions, copolymer microphase separation and blend miscibility.

DPD particles can represent many monomers on a polymer chain; the particles interact through ultrasoft potentials so there is a finite probablity that chains will pass through each other! In this presentation we discuss the advantages and limitations of using DPD to study liquid crystals and polymers.

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Simulation of phase transitions in polymer liquid crystals

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Liquid crystal polymers are copolymers in which mesogenic molecular units are connected either in a backbone polymer chain or as side chains [1]; they have potentially important applications in microelectronics, optical memory devices and high modulus plastics. Experimental work has revealed several interesting phenomena relating to the size of the polymer connections such as the odd-even effect on clearing temperatures, but to date simulations have made a limited impact on the understanding of these complex materials.

The problem is that they are not only atomistically complicated but exhibit complex microphase behaviour due to the interplay of order-disorder and mesophase transitions. Using mesoscale dissipative particle dynamics [2] (DPD) simulations, which ignore all atomistic detail, together with a simple model of rod-shaped mesogens connected by loosely jointed polymer chains, we show the formation of smectic and nematic forms of lamella microphases obtained by cooling a fully disordered system.

Equilibration is achieved very rapidly using DPD and the various transitions can be observed either by heating or cooling. An interesting pseudo-nematic phase can be characterised if the ODT is above the clearing temperature.

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Advanced Monte Carlo simulation methods for colloid-polymer mixtures

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We present Monte Carlo methods that permit the simulation of coarse-grained models of colloid-polymer mixtures (CPM) in a continuum. The sampling of independent configurations is enhanced by using advanced techniques such as configurational bias, single chain rebridging, and also rebridging between two different chains.

We present the application of these methods to the computation of the potential of mean force between pairs of colloids, obtained by inversion of the Ornstein-Zernike equation for the radial distribution function of colloids immersed in the mixture.

We analyze the dependence of this effective interaction in terms of simple scaling arguments.

Finally, we discuss the computation of phase diagrams for CPM by Monte Carlo simulations (both in lattices and the continuum) as well as by thermodynamic perturbation theories.

Multiscale simulation of liquid crystals

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Nematic liquid crystals are characterized by the occurrence of disclination lines, topological defects where the average molecular orientation changes abruptly. Besides their application in displays, recent experiments have shown that liquid crystals permit the detection of ligand-receptor binding by optical amplification.

The optimal design of LC-based biosensors requires to understand the effects of the presence of biomolecules on the structure and dynamics of nematic liquid crystals.

We present a multiscale approach that combines molecular simulation and mesoscale modeling: Monte Carlo simulations are used to study the interactions of dilute colloidal particles, as well as the structure of topological defects; these results compare satisfactorily with the corresponding theoretical calculations at the mesoscale level.

The mesoscale modeling of a multi-particle sensor shows that adsorbed biomolecules modify the relaxation dynamics in the device: at low surface-covering densities, the equilibrium structure is characterized by a slightly perturbed uniform nematic order; at a critical density, the dynamics exhibits a slowdown at late stages, characteristic of the inability of the nematic to arrive at a uniform order.

These results are compared with the experimental observations of the nematic response in biosensors.

Non-Equilibrium Molecular Dynamics (NEMD) studies of the flow properties of polymeric melts

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The flow properties of polymeric melts are studied via NEMD computer simulations. The method is introduced and results are presented for the non-newtonian viscosity and for the normal stress differences of a model polymer melt composed of flexible chain molecules of FENE-type [1,2].

The dependence of these quantities on the chain length is studied. Comparison with Kinetic Theory is made. Furthermore, the shear-flow-induced structural changes as revealed by the static structure factor, the gyration tensor and the flow alignment are analyzed.

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Regular and chaotic rheological behavior of tumbling polymeric liquid crystals.

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The rheological properties of nematic liquid crystalline polymers are strongly affected by the dynamic behavior of the molecular alignment. Starting from a closed nonlinear inhomogeneous relaxation equation for the 5 components of the alignment tensor [1] which, in turn, can be inferred from a generalized Fokker-Planck equation [2], it has recently been demonstrated that the rathercomplex orientation behavior of "tumbling" nematics can even be chaotic [3] in a certain range of the relevant control variables.These are the shear rate and tumbling parameter.

A similar conclusion was reached in [4] where 65 moments were used in a solution of the Fokker-Planck equation. In this talk, the rheological consequences, in particular the shear stress and the normal stress differences are computed and discussed for such a nematic. Long-time averages are evaluated both for imposed constant shear rate and constant shear stress. The time response of the shear stress to step-like and ramp-like shear rates as well as to reversal of the shear rate areanalyzed in the regular and in the irregular, i.e. chaotic regimes.

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Rotation and deformation of polymers in solutions subjected to a shear flow.

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The rotation, the orientation and the conformational changes of flexible chain molecules in a streaming solution are studied by NEMD computer simulations [1] and for a simple modelsystem of a nonlinear elastic dumbbell subjected to a flow field and time-reversible thermostats [2] and twirlers [3].

The similarities and differences of the results inferred from the many particle calculations and from the simple model are outlined. The occurrence of a chaotic behavior for a range of shear rates is discussed.

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Sequence Design in Functional Copolymers: Computer Simulations Intramolecular Ordering in Copolymer Globules

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The possibility of design of sequences of synthetic copolymers in order to achieve desired functional properties is considered. The adopted approach is biomimetic in its nature: we look at the properties of primary structure in biopolymers and try to implement similar ideas in the sequence design of synthetic copolymers. One of the examples corresponds to "protein-like copolymers" which collapse to a nanostructured globule with a well-defined hydrophobic core wrapped in a hydrophilic envelope. These protein-like copolymers can be easily generated in computer simulations.

The real synthetic procedures based on polymer-analogous reactions, on the copolymerization in poor solvent with simultaneous formation of copolymer globule, as well as on the direct solid phase polypeptide synthesis, will be also described. As a result, it becomes possible to synthesize a copolymer macromolecule which undergoes coil-globule transition without simultaneous intermolecular aggregation and precipitation.

The kinetics of the collapse transition of protein-like copolymers is described and compared with the collapse of random and random block copolymers. For the designed copolymers collapse occurs at a markedly higher rate. Still it is possible to select champion “fast folders”. Those normally have larger mean length of hydrophobic and hydrophilic blocks, wider distribution of block length and the average hydrophobicity decreasing towards the chain ends.

The statistical properties of primary sequences of protein-like copolymers designed as described above are considered as well. It is shown, both by computer simulations and by exact analytical calculation that for large globules and flexible polymers such sequences exhibit long-range correlations which can be described by Levy-flight statistics.

The concept of evolution of sequences of synthetic copolymers is introduced, and some of the examples of experimental realization of such evolution are described. The parallels with the evolution of sequences in biopolymers are discussed. Both ascending and descending branches of the evolution of sequences are modeled. It is shown that via evolution of sequences, it is possible to obtain copolymer chains with more perfect statistical characteristics in comparison with the synthetic procedures mentioned above. Thus, such chains are even more designed for implementation of specific functions. As a measure of sequence complexity emerging in the course of evolution, the so-called Jensen-Shannon divergence measure is used. This characteristic correlates well with our intuitive notion of complexity of the sequence, contrary to Shannon entropy or sequence compressibility. For the sequences designed in the course of evolution, the Jensen-Shannon divergence measure exhibits a maximum just at the threshold of the transition towards the evolution degeneracy of sequences.

Other examples of the function-tuned copolymer sequences are considered: copolymers tuned to the adsorption on plane surface, copolymers tuned to absorb small colloidal particles or proteins (molecular dispensers), copolymers which mimic proteins with active enzymatic center etc. One of the most important problems in this field is the design of copolymers capable to recognize certain specific nanopatterns on the surfaces via preferential adsorption on these nanopatterns.

Entangled Polymer Melts and Solutions

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Polymer melts, solutions, and networks display unique (visco)elastic and relaxational properties. Though there is a huge quantitative variation depending on chemical species and e. g. temperature, the general properties are universal.

The presentation will review the role of the fact, that long chain molecules (flexible threads) exhibit special dynamic and elastic properties due to the fact that the threads cannot cut through each other. This is of no relevance for the question of the overall chain conformation.

By comparing analytic theoretical approaches, computer simulations as well as experiments, the effect of conserved topology of linked threads will systematically be isolated and demonstrated. Simulation approaches to study static and dynamic properties of such melts will be discussed in detail. In this context we also show, that the concepts of Gaussian linking numbers and more advanced ones between pairs of closed paths and standard approaches from knot theory are not sufficient to understand the systems, because "many chains" effects are needed to stabilize the complex topological structure of a polymer melt or network.

Employing a new topology conserving approach the entanglement molecular weight for different model systems as well as specific polymers can be determined. To do so the analysis of the melt conformations is sufficient.

Simulations of Polymers:
Link between different scales, energy entropy interplay

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Unlike low molecular weight compounds, polymers have a huge intra-molecular entropy, which is proportional to the molecular weight of the object. This entropy dominates the packing of the beads with each other and the overall conformations. This part of the free energy is generic and qualitatively the same for all polymers, leading to universal static and dynamic properties. It can be understood on a mesoscopic or "scaling" level.

On a microscopic, atomistic scale energies originating from chemical bonds and bead-bead interactions dominate the structure. These energetic contributions differ significantly for different chemical species and have a magnitude also proportional to the polymer molecular weight. Thus both, the energetic and the intra-chain entropic contributions are of the same order. To understand the properties of a given polymer system quantitatively, both aspects have to be properly taken into account. It can be shown that a brute force atomistic simulation of e.g. a polymer melt is neither possible for almost all systems of interest, nor very useful, since most of the generated information is not needed for the quantities of interest.

The lecture gives some examples of attempts to systematically link simulations on different length scales and by this to generate well equilibrated conformations of dense polymer systems. For the example of polycarbonates different modifications are considered. This allows e.g. studies of the vacancy structure and penetrant diffusion in polymer matrices. In a next step specific interactions of bead fragments with metal surfaces have been studied by a combination of ab initio and coarse grained simulations.

Some things we can learn from chemically realistic polymer melt simulations.

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In the last decade chemically realistic and quantitatively correct Molecular Dynamics simulations of polymer melt dynamics have become feasible. These simulations start from well optimized quantum chemistry based force fields.

The most important part of these force fields for the understanding of the relaxation properties of polymer melts are the torsional potentials. I will exemplify the model building for the case of 1,4 polybutadiene. These force fields are then used in Molecular Dynamics simulations which span time scales of 100 nano seconds routinely today for a simulation box of some 5000 force centers.

An analysis of the times series of configurations generated in these simulations allows for the calculations of several experimentally accessible spectra, like, for example, dielectric relaxation, nuclear magnetic resonance and neutron scattering. On small length scales and short time scales these are dependent on the chemical structure of the specific polymer.

The relaxation behavior on large length scales is, however, universal and can be scaled between so different simulation models as chemically realistic MD simulations and Monte Carlo simulations of a coarse-grained polymer lattice model.

Monte Carlo simulations of semi-flexible polymers: From single chains to nematic melts

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The physics of stiff-chain macromolecules for which the chain length L is of the same size or order of magnitude as the persistence length p on which the bending of such a chain occurs is of great importance in the context of bio-macromolecules. DNA typically has a persistence length of around 50 nanometers whereas the one of the building blocks of the cytosceleton, Actin, has a persistence length of around 15 micrometers. We have performed Monte Carlo simulations of a lattice model of such stiff or semi-flexible chains to study the following questions:

1. Under which conditions does a semi-flexible chain collapse into a toroidal structure typical for DNA folded into the cell nucleus and what is the general phase diagram for the coil-globule transition of these semi-flexible chains?

2. Long semi-flexible chain with attractive interactions between them show two types of phase transitions, a liquid-gas transition and an isotropic nematic transition. What type of phase diagram results from the competition between these two phase transitions?

Computational approaches to coarse-graining methods for the description of collective dynamics in nematics and nematic polymers

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We shall consider in our discussion different approaches to coarse-graining descriptions of liquid crystalline fluids, with the purpose of highlighting the potential applications of theoretical and computational mesoscopic treatments to the interpretation of complex behaviors observed for nematics low-weight fluids and nematic polymers, expecially in the framework of shear experiments. Coarse-graining top-to-bottom (i.e. from macroscopic to mesoscopic) and bottom-to-top (from molecular to mesoscopic) methods are nowadays increasing spreading as effective simulation techniques applied profitably to isotropic fluids, but analogous treatments of anisotropic phases are lacking. In order to discuss some examples of coarse-graining techniques applied to nematics, and without any pretence of being truly representative of the field, this presentation will be therefore divided in three parts.

* First a systematic discussion of the basic theoretical foundations of non-linear fluctuations in continuum descriptions of anisotropic liquids will be reviewed, to bridge the stochastic description of compressible isotropic and uniaxial nematic fluids, both in the Langevin and Fokker-Planck formulations

* Next an example of a computational application founded on a coarse-grained Fokker-Planck formulation of a nematic fluid will be discussed, in connection with existing experimental rheological data obtained for nematic and nematic polymers

* Finally a more phenomenological approach, based on a non-standard Dissipative Particle Dynamics description will be described for understanding qualitative aspect of shear properties of nematic polymers.

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Monte Carlo simulations of liquids of mesogenic oligomers

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Monte Carlo simulations have been performed for model liquids of dimers and trimers consisting of rigid cores connected by semiflexible spacers.

Though highly idealized, the models take into account the three principal factors responsible for the onset of nematic order in liquids of segmented-chain oligomers and polymers, i.e. the anisometry of the rigid cores, the anisotropy of their attractive interactions and the intrinsic conformational properties of the molecules under study. In a first set of simulations, the conformation of model trimers has been approximately regulated to mimic idealized systems of rigid cores separated by $(CH_2)_n$ spacers with n odd or even.

The simulated systems show reversible isotropic/nematic phase transitions at well defined temperatures, with odd-even oscillations in good agreement with experiments.

The transitions are coupled with a conformational selection favoring extended conformations in the nematic liquids.

Simulations of model oligomers with conformational properties approximating those of a well characterized series of mesogenic oligoesters are currently underway.

Molecular arrangements in polymer-nanofiller systems

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Polymers containing randomly distributed spherical filler particles have been simulated by Monte Carlo methods for various particle sizes (4 to 28 times the transverse diameter of the polymer chains) and partial volumes of filler (10% to 50%).

The polymer/filler interface consists of densely packed and partly ordered shells of polymer units of thickness nearly twice the diameter of the units. A number of parameters characterizing the molecular arrangements in these systems have been analyzed, leading to a general picture in which the chains are considered to be sequences of interface, bridge and loop segments.

The results can be approximately predicted on a quantitative level using a few simple rules.

It is also shown that phantom chains can be utilized in the simulations, provided that the interaction energy between chains and filler is modified in order to counterbalance the intrinsic tendency of the chain segments to avoid the filler surfaces. This makes possible to study systems that cannot be simulated at full density (i.e. systems with long chains, and/or with large particles and small filling density).

Parallel Computer Simulation Techniques for the Study of Macromolecules

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In recent years two important developments have occurred. At the high-cost end, supercomputers have become parallel computers. The ultra-fast (specialist) processors and the expensive vector-computers of a few years ago, have largely given way to systems which combine extremely large numbers of processors with fast inter-processor communications. At the low-cost end, cheap PC processors have started to dominate the market. This has led to the growth of distributed computing, with PC clusters linked with slow (but very cheap) communications such as simple ethernet. For both of these types of computer systems, new parallel simulation techniques are essential if we are to utilize parallel machines effectively in macromolecular simulations.

This talk will review some of the progress that has been made in developing parallel simulation techniques for macromolecules. It will start with simple methods for molecular dynamics, involving replicated data techniques; and go onto show how parallel performance can be improved by careful load-balancing and reduction of message passing. Domain decomposition MD methods are then presented as a way of reducing message passing further, so that effective parallelization can occur with even the slowest of communication links (ethernet).

Finally, parallel techniques for conducting Monte Carlo are reviewed, and ways of combining parallel methods are presented, which can make effective use of massively parallel architectures without the need to simulate huge systems of molecules.

Computer Simulation of Liquid Crystal Polymers and Dendrimers

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There is considerable interest in the properties of new mesomorphic materials, which are composed of molecules with novel architectures. These include rod-coil molecules, polyphilic molecules, block-copolymers and dendritic molecules. In each of these systems it is possible to combine "molecular building blocks" containing radically different types of molecular interactions (for example aliphatic, aromatic, fluoro, and siloxane-based) to induce microphase separation. This opens up a wide-variety of possibilities for the formation of new self assembled structures.

This paper describes some of our preliminary work to simulate (and attempt to understand) these types of system. Simulations of a side-chain liquid crystalline polymer are described in which a hybrid Gay-Berne/Lennard-Jones model is used. Mesogenic groups are represented by Gay-Berne particles, which are attached to a flexible polymer backbone via a short alkyl spacer. The model system shows spontaneous microphase separation into mesogen-rich and polymer-rich regions, which (under the application of an aligning field) grow to form smectic-A layers. Here, the polymer backbone is sandwiched between mesogenic regions, and becomes surrounded by a sheath composed of the flexible spacer groups.

We also describe a multi-scale approach to the simulation of a polyphilic third generation liquid crystalline dendrimer, in which cyanobiphenyl mesogenic groups are bound to a carbosilane dendritic core via flexible alkyl chains. Fully atomistic simulations predict a structural change for the dendrimer on the application of a mean field ordering potential. Simulations of a hybrid atomistic/Gay-Berne dendrimer in isotropic, nematic and smectic-A liquid crystalline solvents, demonstrate a sphere to rod transition for the dendrimer as the solvent order parameter changes. Finally, simulations of the bulk phase of the dendrimer (employing a coarse-grained sphere/spherocylinders model), demonstrate entropy driven microphase separation into mesogen-rich and dendritic core-rich regions.

Computer simulations of some liquid crystal and polymer liquid crystal models

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We present a brief introduction to the computer simulation of liquid crystalline systems, concentrating on the coarse grained, molecular resolution, level.

We discuss in particular Gay-Berne type models where a mesogenic molecule is replaced by a simple ellipsoidal particle with attractive repulsive interactions and illustrate on one hand the key observables relevant for these anisotropic systems and on the other the variety of phases that can be obtained for rodlike and disclike molecules [1].

We then discuss a possible generalization of the model to the treatment of polymerization in liquid crystals at coarse grain level, with a simple Gay-Berne beads and spring approach.

We discuss a first simple application to the effect of the anisotropic medium on the polymer chains [2].

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Molecular and atomistic simulations of liquid crystals: what can be achieved now?

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In the first lecture we have shown that simple Gay-Berne (GB) models with uniaxial prolate or oblate particles can provide a number of the classical liquid crystalline phases. However, the model has various shortcomings even in a molecular resolution representation. For instance real molecules have dipoles or more complex charge distributions and shapes that can be biaxial or non centrosymmetric, even if the rigid particle approximation is maintained.

We show that generalized GB potentials can yield biaxial, tilted and ferroelectric phases [1,2] that cannot be obtained with the basic GB interactions, thus considerably extending the range of the molecular resolution approach and providing hints for the synthetic chemists wishing to design molecules with an improved chance of yielding mesophases with specific properties of interest (such as ferroelectricity).

The ultimate goal of modelling and simulation is, ideally, the prediction of realistic properties and when the molecular structure of a liquid crystal forming compound is known, one could expect that atomistic modelling and simulations should allow calculating transition temperatures, molecular organization and phase properties. This has not really happened until now, although an increasing number of significant atomistic simulations have started to appear [3]. We show that reasonable estimates for disordering temperatures are now becoming feasible and discuss how this can help our understanding of a classical problem in liquid crystals, the odd-even effect [4].

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Polymer Stabilized Liquid Crystals: Simulation of Physical Properties

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Liquid crystal - polymer dispersions ranging from low liquid crystal content (polymer dispersed liquid crystals) to low polymer content (polymer stabilized systems) are still a fast developing research field.

Recent developments realized in collaboration of groups at University of Bologna, Brown University, and University of Ljubljana are briefly reported.

Ordering in nematic liquid crystals with dispersed polymer networks is studied using Monte Carlo simulations. Results of simulations are used to predict measurable physical properties.

Simulated NMR spectrum, electrical capacitance, and effective birefringence are represented. In particular the effect of network-topography on the field induced switching in nematic cell is simulated.

With increasing network irregularity the transition is less Freedericksz like but nevertheless effectively sharper.