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High-performance polymeric materials such as liquid crystal polymers and polymer nano-particle composites have many military applications. The project aimed to study the mesoscopic structure formation during flow processing and characterization of material properties in solid states. Significant progress has been made to model the materials and to understand their rheological properties in melt or solution processing. Electrical and thermal conduction properties of the nanocomposites are characterized by the low volume fraction asymptotic approach. More anisotropic molecular configuration and their impact to the macroscopic material properties have been investigated. Applications of the models and numerical tools developed for complex fluids are used to important biological applications.

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**MULTISCALE MODELING AND COMPUTATION OF LIQUID CRYSTAL POLYMERS, POLYMER BLENDS, and POLYMER NANOCOMPOSITES: INVESTIGATION OF RHEOLOGY AND MATERTIAL PROPERTIES**

*Final Technical Report*

GRANT NUMBER: F49550-05-1-0025

(Dec. 1, 2004-March 31, 2008)

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**Abstract**

High-performance polymeric materials such as liquid crystal polymers and polymer nano-particle composites have many military applications. The project aimed to study the mesoscopic structure formation during flow processing and characterization of material properties in solid states. Significant progress has been made to model the materials and to understand their rheological properties in melt or solution processing. Electrical and thermal conduction properties of the nanocomposites are characterized by the low volume fraction asymptotic approach. More anisotropic molecular configuration and their impact to the macroscopic material properties have been investigated. Applications of the models and numerical tools developed for complex fluids are used to important biological applications.

The objective of the project is to develop a suite of multiscale models and simulation tools to probe the flowing and solid-state properties of liquid crystal polymer (LCP) and polymer nano-particle (anisotropic particle in particular) composite (PNC) materials guided by Air Force contact Dr. Richard Vaia of material directorate WPAFB. The grant began on December 1, 2004 and ended on March 31, 2008 courtesy of a four-month no-cost extension. The research activities included developing kinetic theories for blends of rigid liquid crystal polymers and flexible polymers as well as theories for biaxial liquid crystals and nano-particle dispersions; studies of kinetic models for extended nematics under the influence of external fields (flow, electric and magnetic field) for external field assisted processing; multiphase flows of rigid LCPs in viscous or polymeric matrices; application of the complex fluids theories and simulation tools to biological settings. In the following, I summarize the completed work and list the publications and synergistic activities during the period. For more technical details, please refer to our publications.

**Structure formation and evolution due to flow-orientation coupling in shear flows of liquid crystal polymers**

The Pi and his collaborators (M. G. Forest, R. Zhou, Z Cui, H. Zhou, X Yang) continued the refined analysis on the extended Doi-Hess kinetic theory for shear flows and general planar linear flows of inhomogeneous liquid crystal polymers. The aim here is to provide a comprehensive understanding of the poly-domain flow behavior as well as the mesoscale structures governed by the kinetic theory and closure models for inhomogeneous LCPs. We focused on multidimensional phenomena where the defect formation and annihilation dominates the mesoscale morphology leading to the experimentally observed optical turbulence. A spatially 2-D kinetic solver is developed to study the multiscale phenomena. Following the monodomain road map, we have identified a variety of temporal-spatial structures and patterns in sheared nematic LCPs of inhomogeneous flows. The newly identified chaotic behavior in monodomains is also observed in the inhomogeneous flow through both temporal and spatial ramifications [4,5,10]. At weak shear, we also examined analytically and numerically the asymptotic behavior of the sheared cholesteric, a nematic LCP exhibiting the helical structure in space, and structure evolution with various physical parameters as well as scaling laws [1,2,3].

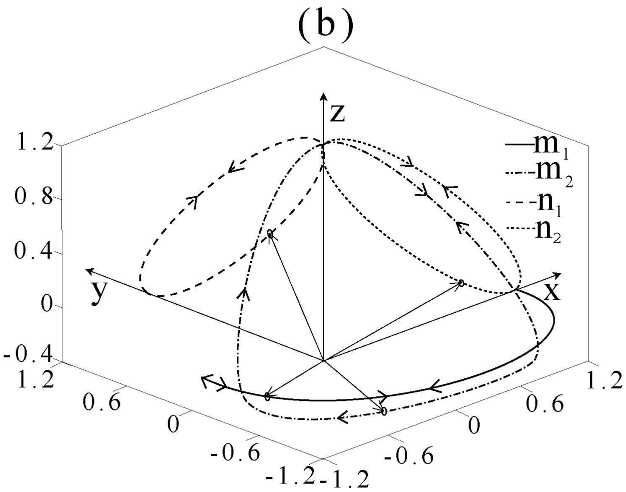
A recent computational study focused on the defect structure in 2-D sheared LCP using the DMG model [11]. A simple scale diagnostic was identified which could lead us to more rewarding systematic investigation of defects in the complex fluids system.

**<u>Material property characterization through mesoscopic structure calculations</u>**

Through interaction with Dr Vaia at WPAFB and joined by Prof. Lipton of LSU, we carried out a series study on the conductivity property of polymer-particle-inclusion nanocomposites. We employed a homogenization technique to arrive at the effective conductivity property of the nanocomposites described by the mesoscopic structure tensor of the nanocomposites. The mesoscopic structure is the output of our nonhomogeneous theory for nanocomposites. The conductivity properties at various material parameter regimes are investigated. Spatially inhomogeneous morphology of the nanocomposites is explored recently giving rise to an effective medium property throughout the physical domain where the medium resides. Ref [14-17].

**<u>Multiscale kinetic theories for flows of biaxial liquid crystal polymers</u>**

Given the rising interests in the modeling of nanofluids of biaxial constituents such as the Banana shaped molecules of liquid crystal polymers, I developed hydrodynamic theories for the biaxial liquid crystal polymer by modeling it as an ellipsoid or a V-shaped rigid body suspended in viscous solvent. The excluded volume interaction potential is calculated from the first principle. The probability density function is sought by a spectral method for the Smoluchowski equation based on the Wigner function expansion. Lower-dimensional approximation to the second moment space or reduced order models is also attempted to resolve the coarse-scale dynamics. We have studied the flow-induced structure transition with a general excluded volume potential and the monodomain structure in sheared biaxial liquid crystals and under imposed external fields like magnetic and electric field [12]. A new time-periodic motion was identified termed as the flutering-kayaking motion whose major director motion is shown in the figure below. More results are being summarized for publication.




**Mathematical study of the fundamental structure in Smoluchowski equation for a general class of intermolecular potential under imposed flow and other external fields**

In this subproject, we examined the impact of the imposed flow and/or external field like electric and magnetic field to the dynamics of rigid extended nematic liquid crystal polymers. We have been working with a general intermolecular potential given by

$$V_i = -kT[\mu E \bullet m + \alpha < m > \bullet m + \frac{3N}{2} < mm > \bullet mm + \frac{\alpha_0}{2} EE : mm],$$

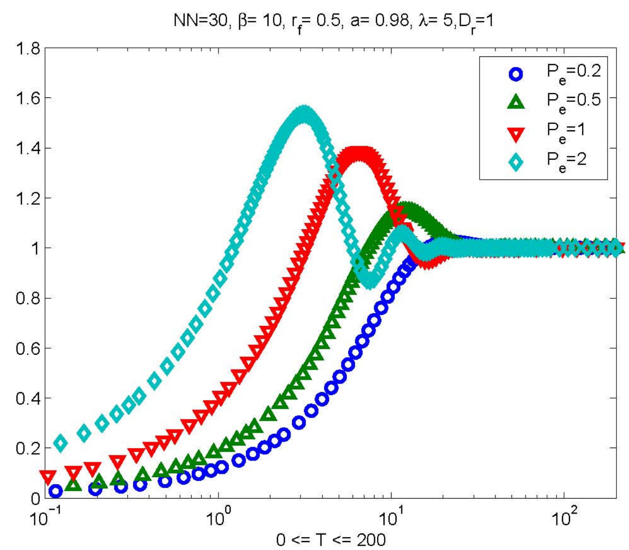
where $\mu$ is the strength of the permanent dipole along the molecular direction m, $\alpha$ is the strength of the induced dipole, N is the strength of the effective excluded volume potential, E is the electric of magnetic field, $\alpha_0$ is the anisotropy of the material, and k is the Boltzmann constant and T is the absolute temperature. This potential models the excluded volume interaction as well as dipolar interaction for extended nematics, including, polar nematics and magnetic dispersions.

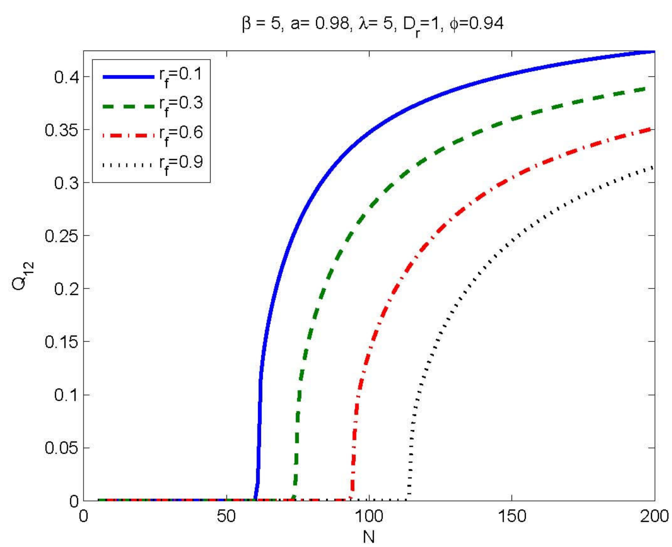
We have used a new reduced-order method to explore the solution of the Smoluchowski equation exactly for imposed potential flows, including elongation and planar extension, etc. In a series of papers [6,7,8,9], we completely characterized the solution structure of the governing Smoluchowski equation with various potentials as well as the flow-orientation diagram in planar linear flows, which encompass many useful rheometric flows. We revealed the mechanism for generating biaxial, polar nematic phases under the influence of mutual molecular interaction and the driven field. Phase transition diagram containing tricritical points and triples points are obtained. These fundamental studies on the solution structure of the Smoluchowski equation shed some new light on the closure approximation for closure models of liquid crystal polymers and nano-dispersions as well as the genesis of the various liquid crystal phases.

**Kinetic theories and rheological prediction for polymer nano-particle composites**

The PI along with his collaborator M. G. Forest have developed a new set of kinetic theories for polymer nano-particle composites accounting for the semiflexibility of the nano-particles such as nanoclays, silicones, etc. as well as the contact interaction between flexible polymers and the nano-particles. These nano-particles can be semiflexible rods or thin platelets. Preliminary results show the impact of the semiflexibility and the contact interaction to the equilibrium phase of the nanocomposites. The first figure below depicts the shear viscosity prediction at a set of selected shear rates. The prediction qualitatively matches the experimental data.

In the next figure, the semiflexibility of the "nanoparticles" or inclusions also affects the phase behavior of the nanocomposites, where $r_f$ denotes the degree of semiflexibility of the nanoparticles (r=0 corresponds to the fully rigid limit). The details are summarized in two papers to be submitted soon.



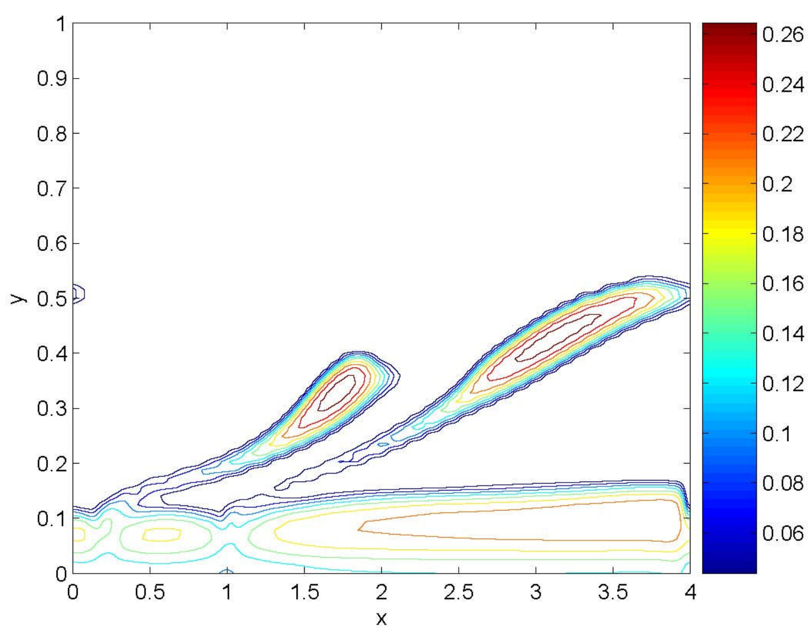



## Modeling blends of liquid crystal polymers and flexible polymers

In collaboration with Prof. Ping Lin of National University of Singapore, we are conducting a series studies on the blends of immiscible liquid crystal polymers and viscous fluids or flexible polymer fluids. Various combinations of the constitutive models for the flexible polymers can be incorporated into the phase-field model for the blends. The goal is to understand the motion of liquid crystal droplets in viscoelastic matrix subject to external shear or pressure. This study would shed light on the mixing of liquid crystal polymers in polymer matrices through external stirring motion. A finite element solver for the flow problem has been implemented and preliminary numerical results are obtained.

## Other applications

The experience and expertise acquired during our studies of complex fluids, especially, the liquid crystal polymer and flowing nanocomposites has enabled us to model multiphase complex fluids both theoretically and numerically using the phase field approach. We have found applications of our models and methodologies in biofilm, a mixture of polymeric network and viscous fluid components comprising of bacteria and nutrient-rich solvent, cell motility, etc. We are applying a coarse-grain dynamical model for semi-flexible polymers to study the self-assembly phenomena in F-actin solution. This could have a potential impact on tissue regeneration for wounded soldiers and fabrication of high performance materials. Figure below depicts the detachment of a biofilm in shear flows.




The research activities on the project funded by the award proceeded smoothly according to the plan. Additional projects closely related to the originally proposed were identified and added to our research activities (like actin self-assembly study and applications to biofilms etc.). The slightly expanded scope of research facilitated our efforts for the overall objective as well as addressing the need of the Air Force.

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**Point of Contact**

Dr. Richard Vaia, AFRL/MLBP, WPAFB, OH, Phone: 937-255-9184, Met him at the workshop on New Challenges in Composite Materials, Dayton, 2005.

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