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**13. SUPPLEMENTARY NOTES**

This is the final technical report.

**14. ABSTRACT**

This contract has led to a design and control capability for high performance, nano-composite materials. Results obtained explicitly link material performance properties to detailed modeling of flow processing. The target materials are nematic polymer nano-composites in which nano-elements are high-aspect-ratio rods or platelets with extreme property contrasts relative to the matrix. Benchmark prototype materials yield striking enhancements in multi-functional properties. A suite of modeling tools for design engineering, which did not exist previously, have been developed. We have developed key theoretical, modeling, and numerical tools for modeling nano-composite permeability to gases or liquids, high electrical conductivity, high and low thermal conductivity, and elastic moduli, and have developed an integrated model and simulation package, capable of direct predictions as well as inverse characterization tools. In this 9month period, we have arrived at the key ingredients for a property control strategy.

**15. SUBJECT TERMS**

Property characterization of nano-rod and nano-platelet composites; conductivity and mechanical property tensors; processing-generated nano-composite property tensors

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# A CONTROL STRATEGY FOR HIGH-PERFORMANCE MACROMOLECULAR MATERIALS

**Contract No. FA9550-06-C-0017**
**Final Technical Report**

**January 4, 2007**

**Submitted by:**

**Nonlinear Control Strategies, Inc.**
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**Principal Investigators: M. Gregory Forest and Jerome V. Moloney**

This report summarizes results obtained on all projects described in the contract. The presentation is built on the interim Progress Report from August 17, 2006, with new results added in the final three months of the contract period.

**Project 1, Phase 1. 2d solvers for the coupled Smoluchowski-Navier-Stokes model.** The 2d spatial code for the Smoluchowski equation coupled to Navier-Stokes is complete, running, and has been benchmarked. This is a critical step in determining robustness and stability of the 1d flow-orientational distribution solutions that we have published in the last 2 years. Figures 1 and 2 are generated by the code.

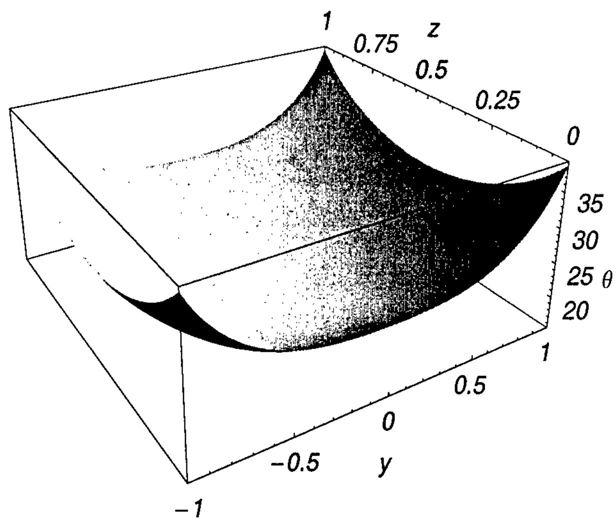



Figure 1. The 2 dimensional variation of the peak direction of the probability distribution function of a steady state structure for a steady shear cell experiment. Each slice z=constant confirms the 1d code structures. The plate speeds and elasticity constants are selected so that the full Smoluchowski-Navier-Stokes system converges to steady state.

This new code both confirms 1d steady state structures (Figure 1) and reveals new features that are inaccessible from 1d models (Figure 2). The materials processing predictions reflected in these Figures are unpublished, but currently in preparation for submission (with R. Zhou, Q. Wang). The algorithm and first benchmark simulations are accepted for publication in the *International Journal of Numerical Analysis and Modeling*, to appear in 2007.

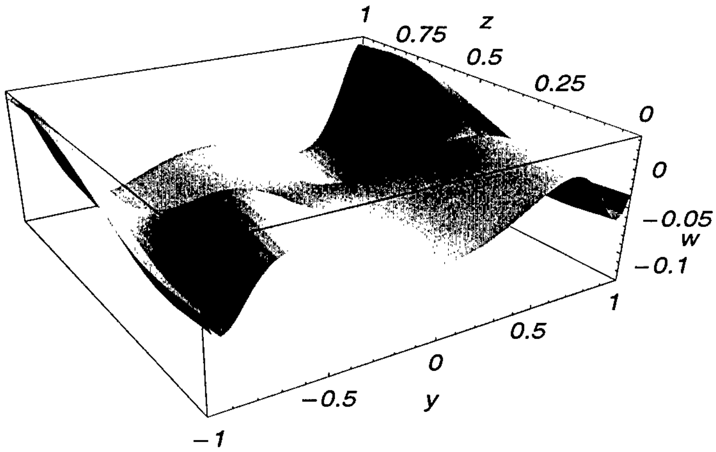



Figure 2. The corresponding 2d vorticity field for the simulation in Figure 1. This result provides new information not contained in 1d model simulations, including evidence of vortical flow generation.

**Project 2, Phase 1. Magnetic fields coupled to planar flows.**
We have extended the model equations at the kinetic and moment closure level to incorporate a coplanar magnetic field to flow processing of nano-particle suspensions where the particles are responsive to magnetic fields. We have developed a "correspondence principle" that identifies a reduced model using a projection method, which allows 6 parameter model dependencies to be explored with 3 parameter simulations. This reduction tool is critical for removal of degeneracies in processing space, which correspond to 3 non-controllable degrees of freedom in material and process parameter space. In a step toward identification of the most sensitive process parameters, we have implemented two codes and applied them to study how imposed coplanar magnetic fields can be used to regularize often complex flow-induced orientational distributions of the nano-particle suspension. One code is a moment closure model, which plays the role of a predictor step since it is $1/15^{th}$ of the order of the kinetic Smoluchowski equation solver, which has also been generalized to incorporate the magnetic field coupling. The predictions of these codes, and the theoretical results that prove the model reduction for both the kinetic and second moment closure models, are

accepted by the *Journal of Rheology* (in press) and *Physics of Fluids* (October, 2007).

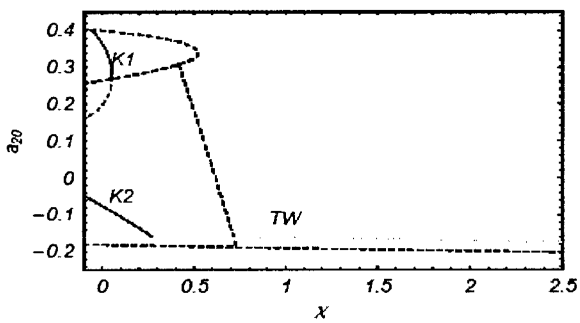



Figure 3. The effect of an imposed magnetic field on a so-called kayaking limit cycle in steady shear flow. The horizontal axis is the magnetic field strength, while the vertical axis is the amplitude of one of the spherical harmonic amplitudes of the probability distribution function.

Figure 3 shows that kayaking limit cycles, a periodic response of the nano-rod dispersion to a steady shear flow which are bi-stable without the magnetic field, survive up to a threshold magnetic field strength. The prediction here is that the magnetic field does not arrest the limit cycles induced by shear, rather the limit cycle collapses onto the shearing plane of the flow and magnetic field, but continues to oscillate in a so-called tumbling orbit. At slightly higher field strengths, tumbling is arrested and a steady state orientational distribution results. These tools are valuable in mapping out the response of nematic rod nano-composites when coupled fields are utilized in processing to control and steer the orientational distribution of the nano-particles. As we have shown in effective property characterizations, certain attractors (kayaking, tumbling, wagging, flow-aligning) are beneficial for specific features of the post-processed film. For example, tumbling promotes films where the principal values of conductivity and mechanical moduli are nearly constant, but the principal axes are highly contrasted. Wagging and kayaking structures have less variability in the principal directions of conductivity and mechanical tensors, but far more contrasts in the principal values along different axes in the material. These and related predictions for all stable shear attractors are presented in the two papers. Other work of the Forest-Wang team has extended the analytical results on kinetic equations in gradient fields, with our current PhD students, which is being prepared for submission now. These results are relevant to the AFOSR goals since they give exact results in special experiments and fields, which are the only sure way to test theory, models, and codes.

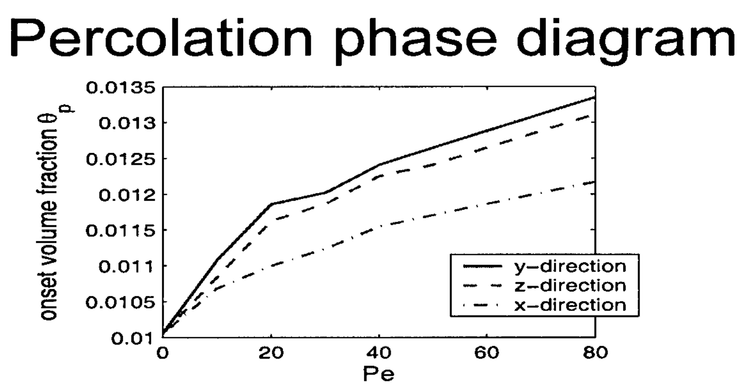
**Phase 3, Project 1. Mechanical property characterization of flow-processed nematic polymer nano-composites.**

We have extended the volume-averaging homogenization results on conductivity to the rank 4 mechanical property tensor. We have shown how flow and volume fraction lead to a wide disparity in the number of independent elasticity constants, and thereby, anisotropic shear and Young moduli. This work is in press in the journal *Continuum*

*Mechanics and Thermodynamics*. It is the first theoretical prediction of volume-averaged mechanical properties of nano-rod composites across processing parameter space.

**Phase 3, Project 2. Percolation in nano-rod composites.**

We have made significant progress on characterization of percolation thresholds versus flow type, flow rate, and volume fraction. The numerical method involves a Monte Carlo algorithm to create realizations of particle composites from the PDFs of the flow phase, following by a data mining algorithm to determine percolation of the nano-rod particle phase. These results were submitted in a short article to Phys. Rev. Letters, and are in preparation for a longer submission, joint with Richard Vaia and Michael Arlen of the Materials Directorate at Wright-Patterson AFB, Dayton, OH. The most intriguing prediction of this work from the point of view of Air Force applications is the ability to control dimensional percolation of bulk films (by choosing the volume fraction and imposed shear rate judiciously). Namely, we predict ranges in processing space where the percolating cluster of nano-rods spans all 3, only 2, or only 1 direction in the film. These results are summarized in the Percolation Phase Diagram below.




``Percolation phase diagram'' of anisotropic percolation thresholds versus volume fraction $\theta_p$ and normalized shear rate Pe, for mono-dispersed rods of aspect ratio 50.

- Above the solid curve, percolating clusters span all 3 directions;
- between the dashed and solid curves, percolating clusters span flow (x) and vorticity (z) direction, without percolation along the flow gradient (y) direction;
- between dashed and dash-dot curve, percolating clusters span the flow direction (x) only;
- below the dash-dot curve, percolation is statistically lost.

**Phase 2: Quench from the liquid to solid phase. Preliminary results with W. Mullins.**

Related work not supported by this contract nor the AFOSR is under way with Bill Mullins, a materials scientist with the Army Research Office in the Research Triangle area nearby Chapel Hill. Mullins has taken our earlier temperature-dependent parametrizations of liquid crystal polymer fiber flows and adapted them to the Doi-Marrucci-Greco flow-orientation tensor model. We have benchmark simulations of the quench phase in the presence of an imposed temperature gradient from the surface of the film. The study of how the orientational distribution modifies and its impact on material property tensors are underway.

**Phase 1, Fundamental Characterization of Nematic Polymer Liquids: inverse characterization of material properties**

A key necessary step in simulations of a flow process is that one knows the material parameters in the viscoelastic constitutive law. For small molecule liquid crystals, this is an advanced field, with 3 decades of literature values for all the Leslie-Ericksen-Frank model parameters for a host of different materials. The analogous tables for large macromolecular suspensions are in short supply, mainly because of a lack of modeling results on the kinetic and second-moment closure models that tell experimentalists the protocols that lead to easy parameter inferences from their data. The Forest group has spent considerable effort in the past year to resolve this problem. A paper that is almost ready for submission with E. Choate (receiving his PhD in May 2007)and Z. Cui (postdoc), both supported in part by AFOSR, provides a significant contribution to this problem. We show how either pressure driven or plate driven experiments can be optimally designed to extract the material properties of the Doi-Marrucci-Greco theory for nematic polymers, and then show the linear viscoelastic properties that are necessary to observe if this theory is accurate. This work will be submitted in the next month to Rheologica Acta. It generalizes our own recent work from homogeneous monodomains to include heterogeneity, and it generalizes the recent work of Rey and de Andrade Lima using the Leslie-Ericksen model for small molecule liquid crystals.

**Pipeline Modeling: Combining flow-orientation distribution codes with property characterization codes.**

One of the key challenges outlined in this contract is the linkage between different phases in the nano-composite materials pipeline, without which there is no way to optimize and control from composition to performance. In a multi-investigator effort with X. Zheng, R. Lipton, R. Zhou, H. Zhou, and Q. Wang, we have made advances in linking our suite of codes. The percolation project above is one example; we populate actual nano-rod dispersions by drawing from the flow-generated PDF from the Doi kinetic theory. H. Zhou and Forest have studied structures in Poiseuille flow numerically and with asymptotic analysis, and then used our homogenization results to predict the effective conductivity tensors generated in pressure-driven flows; this work is to appear in the *Int. J. Numerical Analysis & Modeling.*

**Publications related to and resulting from this contract:**


- Alignment and rheo-oscillator criteria for sheared nematic polymer films in the monolayer limit, (with J. Lee, R. Zhou), Discrete and Continuous Dynamical Systems, Volume 6, 339-356 (2006).

- Anchoring distortions coupled with plane Couette & Poiseuille flows of nematic polymers in viscous solvents: morphology in molecular orientation, stress & flow, (with H. Zhou), Discrete and Continuous Dynamical Systems, Volume 6, 407-425 (2006).

- On weak plane Couette and Poiseuille flows of rigid rod and platelet ensembles, (with Z. Cui, Q. Wang, H. Zhou), SIAM J. Applied Math, Vol. 66, Number 4, 1227-1260 (2006).

- A classical problem revisited: Rheology of nematic polymer monodomains in small amplitude oscillatory shear, (with E. Choate), Rheologica Acta, ISSN: 0035-4511, (Online), March, (2006).

- Nematic liquids in weak capillary Poiseuille flow: structure scaling laws and effective conductivity implications, (with H. Zhou), Int. J. Numerical Analysis & Modeling, to appear (2006).

- Nano-rod suspension flows: a 2D Smoluchowski-Navier-Stokes solver, (with R. Zhou, Q. Wang), Int. J. Numerical Analysis & Modeling, to appear (2006).

- Monodomain dynamics for rigid rod & platelet suspensions in strongly coupled coplanar linear flow and magnetic fields, II: Kinetic theory, (with S. Sircar, Q. Wang, R. Zhou), Physics of Fluids, online October, 2006.

- Monodomain dynamics for rigid rod & platelet suspensions in strongly coupled coplanar linear flow and magnetic fields, (with Q. Wang, R. Zhou), J. Rheology, to appear, 2006.

- Nematic polymer mechanics: flow-induced anisotropy, (with X. Zheng, R. Lipton, R. Zhou), Continuum Mechanics & Thermodynamics, to appear, 2006.

- Anchoring-induced structure transitions of flowing nematic polymers in plane Couette cells, (with H. Zhou, Q. Wang), submitted to Discrete and Continuous Dynamical Systems B, November, 2006.

- Shear-guided anisotropic geometrical percolation in nano-rod ensembles, (with X. Zheng, R. Vaia, M. Arlen), Phys. Rev. Lett., submitted, 2006.

- Linear viscoelasticity of heterogeneous nematic polymers, (with E. Choate, Z. Cui), UNC preprint, to be submitted to Rheol. Acta, 2006.

**AFRL Point of Contact**

Richard Vaia, AFRL/MLBP, Bldg 654, WPAFB, OH, Phone 937-255-9184. Forest lectured in the Polymer Nano-composites Symposium, co-organized by Vaia, March 15, 2005, San Diego, CA. Forest, Vaia, his postdoc Michael Arlen, and X. Zheng have collaborated for the past year on percolation-dominated nano-rod property characterization, combining experiments and theory/modeling/simulation.

Contract FA9550-06-C-0017, Final Technical Report, Submitted by Nonlinear Control Strategies, Inc.

**Transitions**
None as of this date. Potential transitions with Moldflow Corporation, Boston, MA.

**New Discoveries**
None as of this date.