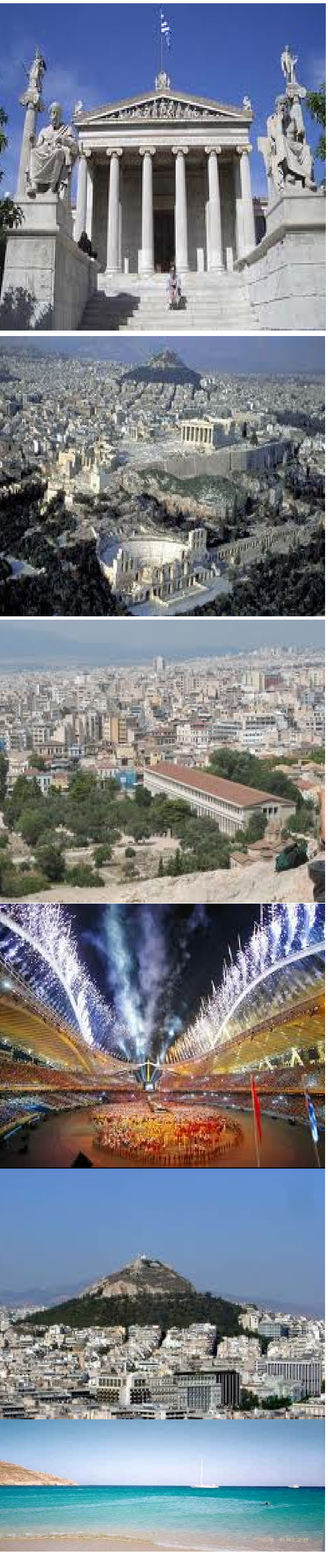

HSR 2011

HELLENIC SOCIETY OF RHEOLOGY

Athens, Greece

June 28-29, 2011

Programme & Abstracts

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Proceedings compiled by Evan Mitsoulis. Cover page designed by Evan Mitsoulis.

CHAIR’S MESSAGE

It is with great pleasure that we welcome all delegates and accompanying persons to the 6th International Meeting of the Hellenic Society of Rheology, HSR 2011, in Athens, Greece. HSR meetings are rotated every 3 years among various locations around Greece and Cyprus. This is the 6th meeting since the foundation of the Society in 1996, when its 1st meeting was held in Nicosia, Cyprus. The 2nd meeting was held in 1998 in Herakleion, Crete, the 3rd meeting in 2001 in Patras, the 4th meeting in 2004 in Athens, and the 5th meeting in 2007 in Rhodes. Athens has been chosen for this meeting, for its central location and ease of access to all participants.

The HSR 2011 Meeting is also a special meeting as it is combined with the 7th GRACM International Congress on Computational Mechanics (GRACM 2011). The HSR meeting starts with sessions on experimental rheology and rheometry and continues with computational rheology, where many Greek rheologists contribute. The HSR Conference includes 2 plenary and 55 oral lectures and 10 posters. The scientific papers will be presented under 8 major themes. We hope that this Conference will promote and facilitate scientific exchange, collaboration and interactions between participants as well as their organisations in advancing science and technology based on rheology.

Athens is reputed as the “cradle of western civilisation” and boasts some of the most important ancient monuments in the world. We hope all international delegates will experience the important attractions that Athens has to offer during their stay in the city.

We thank the NTUA, and in particular the School of Mining Engineering and Metallurgy, for their generous support. We are indebted to the members of the Organising and Scientific Committees and other individuals for their commitment and hard work in order to make this Meeting a successful event.

Prof. Evan Mitsoulis
Conference Chair

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HELLENIC SOCIETY OF RHEOLOGY

The ***Hellenic Society of Rheology (HSR)*** was officially formed on June 16th, 1996, in Athens, Greece, by the Greek judicial authorities having the necessary core of the first 20 founding members. Thus came into fruition the original attempts by the late Professor Tasos Papanastasiou to organize the Greek Rheological community and the many scientists and engineers who practice rheology in their professional careers.

Rheology enters in some form into almost every study of material properties. Many physicists, chemists, engineers, biologists and mathematicians find a common meeting ground in the Society's meetings and publications. It is a small society compared to many others, membership currently being about 40. Membership in HSR is open to all researchers in the field, and to all persons who feel the activities of the Society advance their professional development. The membership represents a wide spectrum of individuals from academic, industrial, and governmental institutions whose activities include both phenomenological and molecular theories, instrumentation, the study of many types of materials such as polymers, metals, petroleum products, rubber, paint, printing ink, ceramics and glass, foods, biological materials, floor preparations and cosmetics, and a wide range of practical applications.

The Hellenic Society of Rheology is one of the fifteen (15) founding members of the *European Society of Rheology*. By virtue of this affiliation, all Members of the Society receive the ESR's Newsletter. The Society is also a member of the International Committee on Rheology, which organizes the *International Congress on Rheology*, held every four years.

Please visit the HSR website at:

http://esperia.iesl.forth.gr/~hsr/HSR.html

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	S.G. Hatzikiriakos
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HSR 2011 Program Summary

Tuesday, June 28, 2011

08:30-09:00	*Registration*
09:00-09:05	*Welcome remarks*
09:05-09:50	**Plenary presentation by Prof. D. Vlassopoulos**
09:50-10:30	**2 presentations**
10:30-11:00	*Coffee break*
11:00-13:00	**4 presentations**
13:00-15:00	*free for lunch*
15:00-16:20	**4 presentations**
16:20-16:40	*Coffee break*
16:40-18:00	**2 presentations + HSR Business Meeting**
18:00-20:30	*Break*
20:00-23:00	*Banquet*

Wednesday, June 29, 2011

08:45-09:30	**Plenary presentation by Prof. Y. Dimakopoulos**
09:30-10:30	**3 presentations**
10:30-11:00	*Coffee break*
11:00-13:00	**5 presentations**
13:00-15:00	*free for lunch*
15:00-16:40	**5 presentations**
16:40-17:00	*Coffee break*
17:00-18:00	**3 presentations**
18:00	*End of Conference*

Total:

1 Plenary presentation by Prof. D. Vlassopoulos (45 min)
1 Plenary presentation by Prof. Y. Dimakopoulos (45 min)
28 oral presentations (20 minutes each)
Posters

Tuesday, June 28, 2011

08:30 Registration

09:00 Welcome Remarks

Morning session I: Rheology and Rheometry

Chair: G.C. Georgiou
Plenary Talk

09:05-9:50 **D. Vlassopoulos**
Structure and viscoelasticity of fluorocarbons at the air/water interface

09:50-10:10 **A.D. Gotsis,** E. Fragkoulis
Bubble growth in a polymeric fluid undergoing a cross-linking reaction

10:10-10:30 H. Anvari Ardakani, S.G. Hatzikiriakos, Th. Zisis, **E. Mitsoulis**
Rheology and processing of toothpaste

10:30-11:00 ***Coffee break***

Morning session II: Rheology and Rheometry

Chair: Ch. Tsenoglou

11:00-11:20 **S. Coppola,** D. Visani, F. Bacchelli
The viscoelastic catenary: fall and rise of polymer filaments

11:20-11:40 **H. Lentzakis,** D. Vlassopoulos
Extensional rheology of model branched polymers

11:40-12:00 **E. Mitsoulis**, S.G. Hatzikiriakos
The effect of slip in the flow of a HDPE melt: experiments and simulations

12:00-12:20 D. Truzzolillo, **D. Vlassopoulos**, M. Gauthier
Star-linear polymer mixtures: a subtle balance between depletion and osmotic shrinkage

13:00-15:00 ***Free for lunch***

Afternoon session I: Structure and Dynamics of Polymers

Chair: A. Gotsis

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Self-assembly, dynamics and kinetics of structure formation in discotic liquid crystals of nano-graphenes

15:20-15:40 **Ch. Tsenoglou**, P. Kiliaris, C.D. Papaspyrides
Assessing the variable molecular size and architecture of poly(ethylene terephthalate) under reactive modification by melt and dilute solution rheology

15:40-16:00 **A. Anastasiou**, C. Baig, V.G. Mavrantzas
Non-equilibrium molecular dynamics simulation of the stretching behavior of adhesive polymers

16:00-16:20 **E. Voyiatzis**, D.N. Theodorou
Viscosity computation of a polystyrene-fullerene nanocomposite system through hierarchical modeling

16:20-16:40 ***Coffee break***

Afternoon session II: Colloids and Suspensions

Chair: D. Vlassopoulos

16:40-17:00 A.S. Poulos, J. Stellbrink, **G. Petekidis**
Nonlinear viscoelasticity and yielding of soft colloidal glasses probed by large amplitude oscillatory shear

17:00-17:20 N. Koumakis, **G. Petekidis**, J. Brady
Yielding of colloidal glasses and gels

17:20-18:00 **HSR Business Meeting**

18:00 *End*

20:00-23:00 *Banquet*

Wednesday, June 29, 2011

Morning Session I: Numerical Simulations

Chair: J. Tsamopoulos

Plenary Talk

08:45-9:30	**Y. Dimakopoulos** *Hemodynamics of the aortic valve: numerical simulation and open issues*
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09:50-10:10	K. Tsiglifis, K. Efthimiou, **N. Pelekasis** *Boundary element simulations of insonated contrast agents – effect of the viscoelastic properties of the coating*
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Morning Session II: Numerical Simulations

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11:40-12:00	**S. Poyiadji**, G.C. Georgiou *Perturbation solutions of weakly compressible, Newtonian Poiseuille flows with slip along the walls*
12:00-12:20	**A.N. Alexandrou,** G.C. Florides, G.C. Georgiou *Squeezing of a finite amount of viscoplastic material exhibiting thixotropy*
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Afternoon Session I: Molecular Modeling

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15:20-15:40	V**. Harmandaris**, C. Baig *Structure and dynamics of non-equilibrium polymer melts through hierarchical multi-scale dynamic simulations*

15:40-16:00	**S.D. Anogiannakis**, C. Tzoumanekas, B. Rousseau, D.N. Theodorou *Primitive path dynamics and contour length fluctuations in entangled polymer melts: a molecular simulation study*
16:00-16:20	**A. Morozinis,** C. Tzoumanekas, D.N. Theodorou *Molecular modeling of cavitation in polymer melts and rubbers*
16:20-16:40	**A.N. Rissanou**, V.A. Harmandaris, D. Vlassopoulos, C.N. Likos *Effective interaction between diblock-arm star copolymers: a molecular dynamics study*
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Afternoon Session II: Molecular Modeling

Chair: G. Petekidis

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17:20-17:40	**P.S. Stephanou**, G. Tsolou, N. Stratikis, C. Baig, V.G. Mavrantzas *Rouse theory for polymer rings and comparison with atomistic molecular dynamics simulations*
17:40-18:00	**P.S. Stephanou**, C. Baig, G. Tsolou, M. Kröger, V.G. Mavrantzas *Quantifying chain reptation in entangled polymer melts: topological and dynamical mapping of atomistic simulation results onto the tube model*
18:00	*End*

PLENARY LECTURES

Structure and Viscoelasticity of Fluorocarbons at the Air/Water Interface

L. de Viguerie[1], C. Klein[1], U. Jonas[1], and D.Vlassopoulos[1, 2]

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[2]University of Crete, Department of Materials Science and Technology, Heraklion, Crete, Greece

We present our first efforts towards interfacial rheology and structure, aiming at elucidating the role of confinement. In particular, we investigate the structure and viscoelastic properties of semifluorinated alkanes $F(CF_2)_n(CH_2)_mH$ of varying architecture and symmetry, spread on the air-water interface. Langmuir monolayers form surface micelles which have different shape and organization. The fluorocarbon films exhibited a solid-like viscoelastic response throughout the whole range of surface pressures studies. However, the details of the response depend on the molecular features of the fluorocarbon constituent of the surface micelle, and hence, one can tailor at molecular level the film rheology from glass-like to gel-like, taking analogies to the respective bulk response. We also discuss perspectives that will allow tackling nonlinear rheological properties of such types of monolayers.

Work in collaboration with R. Keller, R. Berger, C. G. Clark, K. Müllen (Max-Planck Institute for Polymer Researc, Mainz, Germany) and T. Geue (PIS Switzerland)

[1] L. de Viguerie, R. Keller, U. Jonas, R. Berger, C. G. Clark, Jr., K. Müllen, C. Klein, T. Geue, D. Vlassopoulos, *Langmuir*, 2011
[2] C. O. Klein, L. de Viguerie, C. Christopoulou, U. Jonas, C. G. Clark, Jr., K. Müllen, D. Vlassopoulos, *Soft Matter* 2011

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Hemodynamics of the Aortic Valve: Numerical Simulation and Open Issues

Yannis Dimakopoulos

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We study numerically the nonlinear interaction of a three-dimensional representation of an aortic heart valve, composed of three hyperelastic leaflets of finite density attached to a stented vessel under physiological flow conditions. Blood flow is caused by a time varying pressure gradient that mimics that of the aortic valve and corresponds to high values of the Reynolds number. Here, we fully account for the shear-thinning response of the blood [1], and large deformations of the leaflets, by solving the momentum and mass balances for both phases. The mixed finite element/Galerkin method along with linear discontinuous Lagrange multipliers for coupling the fluid and elastic domains are adopted [2]. Moreover, a series of challenging numerical issues such as the finite length of the computational domain and the conditions that should be imposed on its inflow/outflow boundaries, the accurate time integration of the parabolic and hyperbolic momentum equations, and the non-conforming mesh refinement in part of the domain are successfully addressed. Calculations for the velocity and the shear stress fields of the blood reveal that boundary layers appear on both sides of a leaflet. The one along the ventricular side transfers blood with high momentum from the core region of the vessel to the annulus or the sinusoidal expansion, causing the continuous development of flow instabilities. At peak systole vortices are convected in the flow direction along the annulus of the vessel, while during the closure stage of the valve an extremely large vortex develops in each half of the flow domain [3].

REFERENCES

[1] Gijsen FJH, Allanic E, Van De Vosse FN, Janssen JD. 1999. The influence of the non-Newtonian properties of blood on the flow in large arteries: Unsteady flow in a 90°curved tube. *J. Biomech.* 32 (7): 705-713.

[2] Baaijens FPT. 2001. A fictitious domain/mortar element method for fluid-structure interaction. Int. J. Numer. Meth. Fluids 35 (7): 743-761.

[3] Dimakopoulos, Y., Bogaerds, A.C.B., Anderson, P., Hulsen, M.A, and Baaijens, F.P.T., accepted for publication in Computer Methods in Biomechanics and Biomedical Engineering (2011).

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ORAL CONTRIBUTIONS

Bubble Growth in a Polymeric Fluid Undergoing a Cross-Linking Reaction

Alexandros D. Gotsis and Emanuel Fragkoulis

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This is a study of the growth of a bubble within a polymeric fluid that undergoes crosslinking reaction (vulcanisation). The changes in the viscoelasticity of the polymer melt are estimated by expanding the theory of Tsenoglou et al. (2006)[1] to a crosslinking system. The goal of the project is to generate knowledge that can be applied in the manufacturing of the rubber foam used for insulation.

The (single) bubble growth is initiated by the explosive decompostion of a grain of the foaming agent. The vulcanisation reaction results initially in evolving changes in the relaxation spectrum of the polymer and the degree of branching. Both of these can change the elongational viscosity of the melt and, especially, its strain hardening behaviour. The changing viscoelasticity of the melt influences the growth rate of the bubbles and their final size. At the end of the process, when the crosslinking is complete, the growth of the bubbles stops.

The density of the produced foam depends on the foaming agent, the rate of the vulcanisation reaction, the foaming agent grain size and the initial relaxation spectrum of the polymer.

[1] C.J. Tsenoglou, E. Voyiatzis and A.D. Gotsis, J.Non Newt.Fl., 138:33-43 (2006)

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Rheology and Processing of Toothpaste

H. Anvari Ardakani[1], S.G. Hatzikiriakos[1], Th. Zisis[2], E. Mitsoulis[2]

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Commercial toothpaste is investigated in this work as a model paste system to study its processing characteristics in capillary flow using various dies. Its rheological behaviour has been determined as that of a yield-stress, thixotropic material with time dependent behaviour. The rheological data obtained from a parallel plate rheometer were used to formulate a constitutive equation that is a Herschel-Bulkley model with a structural parameter which obeys a kinetic equation, typically used to model thixotropy. The predictive capabilities of this model is tested against capillary data for a variety of capillary dies having different length-to-diameter ratios (*L/D*).

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The Viscoelastic Catenary: Fall and Rise of Polymer Filaments

Salvatore Coppola, Danilo Visani, Fabio Bacchelli

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Extensional flow of polymer melts is of major importance in a wide range of applications and processing technologies. In particular, complex extensional creep and recoil flows controlled by gravity and polymer elasticity are encountered in a number of practical situations typical of elastomer industry (e.g. cold flow during the storage period, sagging and shape distortions after extrusion of slender elastomer products). Understanding the sagging phenomenon induced by gravity on slender viscoelastic polymer samples, like filaments and thin films, is therefore not only a scientific challenge but also an important technological goal.

Inspired by the experimental work by Roy et al. [J. Fluid Mech. (2006) 563, 283-292] on a viscoelastic Boger fluid, we investigated a set of entangled Polybutadiene samples with varying molecular architecture. Polymer samples were extruded in a Goettfert capillary rheometer in order to obtain filaments. The specimens were then allowed to relax for 24 hours in water bath in order to prevent shape distortion during this stage.

Horizontal polymer filaments supported at both ends, have been stretched moving the supports apart. The filaments were then allowed sagging under the effect of gravity. After a certain sagging period, the supports were moved again to their original positions. In this way, the abrupt change of boundary conditions and filament shape originated an imbalance between elastic and gravity forces. The polymer filament started therefore rising driven by its elasticity. Different conditions of stretching ratio and sagging time have been used.

The experimental results were compared with literature results and predictions regarding the sagging [Brochard-Wyart and De Gennes, EPL (2007) 80, 36001; Roy et al., J. Fluid Mech. (2006) 563, 283-292] and the rising stage [Roy et al., J. Fluid Mech. (2006) 563, 283-292].

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Extensional Rheology of Model Branched Polymers

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The effects of polymer architecture on the elongational properties of branched polymers is still not completely understood. The lack of knowledge of the effect of branching is a crucial problem for industrial polymers where processes are characterized by strongly non-linear extensional flows.

In this work, we use the H-shaped and comb architecture to investigate the influence of molecular characteristics such as the number of branch points, the length of the branches and the length of the backbone on the elongational behavior. The comb architecture consists of a linear chain backbone with multiple branch points of equal length randomly distributed and attached to the backbone.

Small amplitude oscillatory shear experiments (SAOS) and time temperature superposition (TTS) were performed to characterize the linear viscoelastic response of the branched polymers. Uniaxial extensional rheology was carried out using the SER (Xpansion instruments) fitted into an ARES rheometer. The elongational data at 170°C for polystyrene and 0°C for polyisoprene was found to fit very well to the linear viscoelastic envelope (LVE).

The results show that an increase of the length of backbone and branches, as well as the number of branches, yields an increased effect of strain hardening. They also reveal distinct signatures of the different molecular characteristics of the branched polymers, suggesting ways for tailoring the rheology by designing appropriate macromolecules. In order to model the elongational rheology of the combs, we use the differential pom-pom model first proposed by McLeish and Larson which was further advanced by Blackwell et al.

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The Effect of Slip in the Flow of a HDPE Melt: Experiments and Simulations

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The capillary flow of a high-density poly-ethylene (HDPE) melt was studied both experimentally and numerically. The excess pressure drop due to entry (Bagley correction), the compressibility, the effect of pressure and temperature on viscosity, and the slip effects on the capillary data analysis have been examined. Using a series of capillary dies having different diameters, *D*, and length-to-diameter *L/D* ratios, a full rheological characterization has been carried out, and the experimental data have been fitted both with a viscous model (Cross) and a viscoelastic one (the Kaye - Bernstein, Kearsley, Zapas / Papanastasiou, Scriven, Macosko or K-BKZ/PSM model). Particular emphasis has been placed on the effects of wall slip (significant for HDPE). For the viscous model, the viscosity is a function of both temperature and pressure. For the viscoelastic K-BKZ model, the time-temperature shifting concept has been used for the non-isothermal calculations, while the time-pressure shifting concept has been used to shift the relaxation moduli for the pressure-dependence effect. It was found that only the viscoelastic simulations were capable of reproducing the experimental data well. On the other hand, viscous modelling underestimates the pressures drops, especially at the higher apparent shear rates and *L/D* ratios. It is concluded that wall slip effects are significant for HDPE flow, whereas viscous heating is not.

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Star-Linear Polymer Mixtures: A Subtle Balance between Depletion and Osmotic Shrinkage

Domenico Truzzolillo[1], Dimitris Vlassopoulos[1, 2] and Mario Gauthier[3]

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A challenge with the liquid-solid transitions is how to achieve their molecular control that would have a significant scientific and technological impact paving the way for the design of soft materials with desired properties. Mixtures of star polymers with linear polymers are an obvious choice (as many soft matter systems occur as mixtures), which however have been only partially investigated [1]. Via linear and nonlinear rheological measurements we are investigating the high concentration linear chains' region of the phase diagram in order to shed light on the possible presence of re-entrances (liquid-to-solid) or solid-to-solid transition for high molecular weights of chains. We found the lack of the attractive glassy phase for high concentration of chains (depletants) for "intermediate" size ratios ($q = 0.17$), whose addition in the concentrated star polymer solution produces the melting of the glass, establishing that the liquid phase extends up to the "nanocomposite-limit" where the star and linear polymer melts are merged.
We also performed rheological measurements on star/linear polymer mixtures diluting the glassy phase of star polymers using different polymer melts. Both the linear (frequency dependence of the complex modulus $G^*(\omega)$) and non linear rheological properties of the mixtures (post yielding power law behaviour of $G'(\gamma)$ and $G''(\gamma)$, extension of the linear regime and Fourier spectrum of stress waveforms at high strain amplitude) clearly show the existence of a critical concentration of chains above which they start to strongly dominate the fastest modes of the material.

Financial support of Marie Curie-Initial Training Net-work (ITN-COMPLOIDS) is gratefully acknowledged.

[1] E. Stiakakis, D. Vlassopoulos, C. N. Likos, J. Roovers, and G. Meier, Phys. Rev. Lett.,89 20, 208302, (2002).

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Self-Assembly, Dynamics and Kinetics of Structure Formation in Discotic Liquid Crystals of Nano-Graphenes

C. Grigoriadis[a], G. Floudas[a], N. Haase[b], K. Muellen[b]

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Discotic liquid crystals (DLC), consisting of rigid disk-shaped aromatic cores and disordered alkyl substituents tend to organize into columnar supramolecular structures. Their self-assembly is driven by noncovalent intermolecular interactions favoring the π-stacking of aromatic cores and the unfavorable interactions between the cores and the alkyl chains leading to nanophase separation.[1] The role of aliphatic chains is also important as they provide with the required solubility and further impart a rich thermotropic behavior and fast molecular dynamics.[2] X-ray scattering revealed two main columnar structures in HBCs: a liquid crystalline phase (Col_h) at higher temperatures composed of columns that are further organized in a hexagonal lattice and a crystalline phase (C_r) at lower temperatures composed of columns of tilted disks (i.e. "herring bone") in a monoclinic unit cell. Applications of DLC as nanoscale conductive devices rely on the optimal stacking of the aromatic cores that allow for charge carrier mobility along the columnar axis (molecular wires). Herein we report on the effect of molecular structure on the thermodynamics,[4] self-assembly,[3,4] the hierarchy of dynamics,[3] the kinetics of structure formation[6] and the viscoelastic properties of a class of DLC, the hexa-peri-hexabenzocorenes.

[1] Wu, J.; Pisula, W. and Müllen, K. *Chem. Rev.* **2007**, *107*, 718-747.
[2] de Gennes, P.G. *J. Phys. Lett.* **1983**, *44*, 657 – 664.
[3] Elmahdy M. M. et al *Phys. Rev. Lett.* **2008**, *100*, 107801-4.
[4] Elmahdy M. M. et al *J. Am. Chem. Soc.* **2008**, *130*, 5311-5319.
[5] Grigoriadis et al *Adv. Mater.* **2010**, *22*, 1403-1406.
[6] Elmahdy M.M. et al *J. Chem. Phys.* **2009**, *131*, 114704-9.

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Assessing the Variable Molecular Size and Architecture of Poly(ethylene terephthalate) under Reactive Modification, by Melt and Dilute Solution Rheology

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Reactive modification by means of coupling agents constitutes an attractive and relatively inexpensive method for tailoring processing characteristics and end-product properties of pristine or recycled linear polymers. The modification usually causes chain extension, broadens the molecular weight distribution and induces long chain branching. By increasing the "melt strength", these changes improve the processablility of the polymer in foaming, thermoforming or blow molding processes. In the case of recyclates, they also reverse degradation caused by prior use.

Monitoring the evolving molecular architecture is essential in controlling and optimizing reactive modification. Yet, this is an almost impossible task when the use of conventional spectroscopic (NMR, IR) or chromatographic (SEC) methods is attempted. A much more convenient method is hereby proposed that utilizes readily accessible melt and dilute solution viscosity data; it is applied in deciphering transfomations in molecular architecture and size occuring on of an originally linear Poly(ethylene terephthalate) (PET) during the early stages of reactive extrusion modification.

Based on the chemical capabilities of the modifying agent, we first assume a plausible senario for the shape and size variation, and relative difficulty of the new polymers formed. We then construct expressions for the evolving melt and intrinsic viscosity of the reacting PET, which in essence, is a mixture of linear and star-branched molecules in ever changing proportions.

The model is tested using two independent sets of viscometric data by Incarnato et al. and Japon et al.; these data refer to PET modified at various degrees with the help of two different tetrafunctional chain extenders: pyromellitic dianhydride and tetraglycidyl diamino diphenyl methane. For both sets of data, there is quantitative agreement between the two methods proposed here in estimating the composition of the various types of PET species formed.

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Non-Equilibrium Molecular Dynamics Simulation of the Stretching Behavior of Adhesive Polymers

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Based on principles of statistical mechanics [1], we have developed a generalized non-equilibrium molecular dynamics (NEMD) algorithm for the molecular simulation of the stretching deformation [2] of adhesive polymers adsorbed on solid substrates. The simulations are carried out in the $NP_{xx}L_{yy}P_{zz}T$ statistical ensemble [3-4], where N denotes the number of interacting atomistic units in the system, P_{ii} the normal pressure in the i-direction, L_y the box dimension along the stretching (y-) direction, and T the temperature. Such an ensemble allows one to simulate a sample confined between two parallel substrates under conditions of uniaxial deformation, since one has full control on the length of the simulation cell along y [5].

To test the code we employed it first in exploratory simulations with three linear polyethylene (PE) melts (a 240-chain $C_{50}H_{102}$ system at density ρ=0.74 g/cm3, a 216-chain $C_{178}H_{358}$ system at density ρ=0.75 g/cm3, and a 216-chain $C_{400}H_{802}$ system at density ρ=0.76 g/cm3) [6], all of them confined between two graphitic surfaces. The three systems were subjected to uniaxial elongation along the y-direction at T=450 K in the $NP_{xx}L_yP_{zz}T$ statistical ensemble by pulling the upper substrate along the y-direction at constant velocity. The lateral values of the pressure (i.e., along the x- and z- directions) were both set equal to 1 atm. As an example of the quality of the results that can be obtained by such a simulation experiment, we mention that for the C_{178} PE system subjected to a stretching rate that corresponds to a Weisenberg number (Wi) equal to 1000, several cavities formed inside the system after approximately 14 ps, which eventually led to crazing and fracture of the material.

Results will also be presented from corrseponding deformation simulations not with PE but with model acrylic adhesives, such as random copolymers of n-butyl acrylate with a short side-chain acrylic like methyl acrylate and acrylic acid.

References

[1] M.Kröger, W.Loose, S.Hess, *J.Rheol.* 37, 1057-1079, **1993**.
[2] C.Baig, B.Jiang, B.J.Edwards, D.J.Keffer, H.D.Cochran, *J.Rheol* .50, 625-640, **2006**.
[3] G.J. Martyna, D.J. Tobias, M.L. Klein, *J. Chem. Phys.* 101, 4177-4189, **1994**.
[4] D.J. Keffer, C. Baig, P. Adhangale, B.J. Edwards, *Molec. Simul.* 32, 345-356, **2006**.
[5] J,M.Kim, D.J. Keffer, M. Kroger, B.J. Edwards, *J.Non-Newt. Fluid Mech.* 152, 168-183, **2008**.
[6] C.Baig, V.G. Mavrantzas, M. Kröger, *Macromolecules* 43, 6886-6902, **2010**.

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Viscosity Computation of a Polystyrene-Fullerene Nanocomposite System through Hierarchical Modeling

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It has been recently reported in the literature that dispersion of fullerenes C60 in a long chain polystyrene matrix results in a non-Einstein-like decrease in viscosity (MacKay et al Nature 2 (2003) 762). This behavior has been attributed to the confinement and surface effects, brought about by the inclusion of fullerenes, since the entanglements seem to be unaffected. The scope of this paper is to investigate computationally this intriguing phenomenon. A hierarchical approach has been used for the reported simulation. The system is first thoroughly equilibrated in a coarse grained level through advanced connectivity altering Monte Carlo moves. It is subsequently mapped, based on a purely geometrical procedure, to a more detailed united-atom representation. The atomistic structure is relaxed through flip Monte Carlo moves. In the final step, the system is subjected to molecular dynamics simulations. The viscosity of the system is calculated by the Green-Kubo relationship.

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Nonlinear Viscoelasticity and Yielding of Soft Colloidal Glasses Probed by Large Amplitude Oscillatory Shear

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A colloidal glass at rest behaves like a soft solid, with the elastic modulus G' larger than the viscous modulus G" at all accessible frequencies. However, the same material will flow when subjected to a strain (or stress) that exceeds yielding. Beyond this shear-induced solid-to-liquid transition, the soft glass exhibits complex non-linear viscoelasticity that is still poorly understood.

Here we study by large amplitude oscillatory shear (LAOS) experiments the yielding and non-linear viscoelasticity of model colloidal glasses, formed by diblock copolymer micelles [1]. As the amplitude of oscillation is increased, the stress response becomes progressively less sinusoidal. The complex stress waveforms are decomposed by Fourier analysis into a fundamental frequency and higher harmonics, following Wilhelm et al. [2], or equivalently into elastic and viscous parts and orthogonal sets of Chebyshev polynomials [3, 4]. These decompositions enable us to map out the rich phenomenology of non-linear rheological behaviour. Thus, as the oscillation amplitude is increased, the linear viscoelastic response changes to a strain hardening intracycle response (intermediate amplitudes), to a shear thinning intracycle response (large amplitudes). The LAOS results on soft micelles are compared to previous results on hard spheres and deformable soft particles with the purpose of contributing to the general understanding of the yielding process in soft matter systems. Moreover, some limitations of the current analysis methods of LAOS experiments are presented. Finally, we propose alternative methods of looking at LAOS experimental results, which provide additional physical insight.

[1] F. Renou, J. Stellbrink, and G. Petekidis, J. Rheol. **54**, 1219 (2010).
[2] M. Wilhelm, D. Maring, and H. W. Spiess, Rheologica Acta **37**, 399 (1998).
[3] K. S. Cho *et al.*, J. Rheol. **49**, 747 (2005).
[4] R. H. Ewoldt, A. E. Hosoi, and G. H. McKinley, J. Rheol. **52**, 1427 (2008).

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Yielding of Colloidal Glasses and Gels

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By adding attractions to a simple colloidal hard sphere glass in the form of a short range depletion, the glass turns into an ergodic liquid, followed by a re-entrant transition to an attractive glass[1]. Simple glasses exhibit a single step yielding under oscillatory or steady shear that is related with the breaking of the first neighbour cage at a strain corresponding to its maximum distortion, 10%-15% strain. However, when strong attractions are added the system yields in a two step manner. It has been proposed that these processes reflect an initial particle bond breaking at low strains and a subsequent breaking of an attractive cage at larger strains[2].

Here we attempt to elucidate the origin of the two step yielding by examining the rheological response of samples with the same interparticle attraction ranging from high volume fraction attractive glasses to low volume fraction colloidal gels ($0.1<\varphi<0.6$). We find that the transition takes place gradually with the cage breaking process being substituted by a cluster dominated process as the volume fraction is decreased, leading to larger yield strains[3].

Rheological measurements are complemented by steady shear Brownian Dynamics simulations of the gel state in order to gain insight on the structural changes that occur during yielding. It is found that the structure of the steady state under shear and after cessation are highly dependent on the shear rate, with low rates tending to increase the structural inhomogenieties compared to rest, while high rates "rejuvenate" the system by breaking up all heterogeneous structure.

[1] K. N. Pham, A. M. Puertas, J. Bergenholtz, S. U. Egelhaaf, A. Moussaïd, P. N. Pusey, A. B. Schofield, M. E. Cates, H. Fuchs and W. C. K. Poon, Science, 2002, 296, 104-106.
[2] K. N. Pham, G. Petekidis, D. Vlassopoulos, S. U. Egelhaaf, W. C. K. Poon and P. N. Pusey, Journal of Rheology, 2008, 52, 649-67.
[3] N. Koumakis and G. Petekidis, Softmatter, 2011(Submitted)

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Statistics in Polymer-Modified Channel Flow Turbulence

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In an effort to further understand the impact of viscoelasticity in modifying inertial turbulence, leading to drag reduction, we present here further statistical evaluation of velocity data collected during large scale numerical simulations of turbulent viscoelastic flow in a channel using the Giesekus constitutive model. More specifically, we examine the way the single and joint probability distribution functions (PDF) of the velocity and velocity derivatives are changed at various distances from the wall and the impact to the corresponding 3rd and 4th moments.
Those PDFs were studied in the past primarily in Newtonian turbulence were they have been found to significantly depart from normal (Gaussian) statistics, as a result, in part, of the intermittency in the flow and the influence of coherent motions on local statistics. Just last year we have reported their study with the presence of polymers and found that those nonGaussian characteristics were even more pronounced, in accordance to the higher intermittency of viscoelastic turbulent flow(1). In the present work we further quantify these polymeric effects on the velocity and velocity derivatives PDFs. For the first time, we focused on the shape of the most pronounced nonGaussian effects, the “fat” tails. As a result to “fat” tails, the probability of otherwise characterized as very improbable events (excursions tens of standard deviations away from the mean) become for these particular distributions much more likely and fairly plausible. Whereas before the analysis was based on an ad-hoc standard histogram procedure, which is for these rare events full of noise and ambiguity, we developed here a much more systematic procedure based on an analysis of the cumulative probability functions and on the implementation of rigorous statistical criteria for rare events, like the Hill estimator. We show that, with viscoelasticity and at certain locations near the wall, the PDFs exhibit “fat” tails falling with a power law and sufficiently slow so that some of their higher moments (above 3) are not even finite. The more general implications of this work to the modeling of viscoelastic turbulence are going to be underlined.

(1) G. Samanta, K.D. Housiadas, R.A. Handler and A.N. Beris, 2009, “Effects of Viscoelasticity on the Probability Density Functions in Turbulent Channel Flow,” Phys. Fluids, 21: article 115106.

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Boundary Element Simulations of Insonated Contrast Agents – Effect of the Viscoelastic Properties of the Coating

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Contrast agents are known to exhibit dynamic patterns such as thresholding, compression only behavior, diffusion and deflation, shape deformation, buckling, jetting and break-up, not all of which can be adequately predicted based on a single model describing the mechanics of the coating. The effect of shell elasticity and viscosity as well as their nonlinear evolution with varying amplitude and frequency of the acoustic disturbance is studied against the above patterns, first in the context of spherosymmetric pulsations. The superiority of strain softening models is discussed and future directions are provided.

Next the dynamics of axisymmetric deformations is studied subject to different constitutive laws for the coating and the possibility for resonance is investigated. The boundary element methodology is adopted for simulating free pulsations of a contrast agent subject to acoustic disturbances and it is seen that strain softening shells exhibit saturated pulsations in the region where linear stability analysis predicts unstable growth of shape modes via harmonic and subharmonic resonance. The onset of instability is enhanced for pre-stressed coatings that arise when gas diffuses out of the shell. On the contrary strain hardening shells almost invariably lead to break-up when growth of shape modes is present.

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The Free Boundary Condition in Viscoelastic Flow Simulations

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The Free (or Open) Boundary Condition (FBC, OBC) was proposed in 1992 by Papanastasiou et al. [1] to correctly impose outlet boundary conditions in arbitrarily truncated domains. In two benchmark problems of the early 1990's, the FBC was found to give excellent results when compared with solutions from long untruncated domains.

In the present work, the FBC is re-examined in the 4:1 abrupt contraction problem, a simple benchmark problem in viscoelastic simulations. The FBC was found to work beautifully for Newtonian fluids under non-isothermal conditions, for integral Maxwell fluids (UCM model) under isothermal or non-isothermal conditions, and for explicit differential equations of the CEF type with or without a second normal stress difference N_2.

However, problems have appeared with the K-BKZ integral model with a non-zero N_2 or with domains truncated too short. These problems had also appeared earlier with the differential Giesekus model [2] and were successfully resolved by assuming at the outlet that $dv_z/dz=0$. Some thoughts are given about the interpretation of these effects, which have not been addressed before.

[1] T.C. Papanastasiou, N. Malamataris, K. Ellwood, A new outflow boundary condition, Int. J. Numer. Meth. Fluids, 14 (1992) 587-608.

[2] Y. Dimakopoulos, PhD Thesis, Univ. Patras, Greece (2003)

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Wall Elasticity Effects to the Outlet Flow Conditions in Blood Flow Simulations through Asymmetric Arterial Bifurcations

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In a previous publication [Johnson DA, Naik UP, Beris AN, 2010, Int J Numer Meth Fluids, DOI: 10.1002/fld.2319] we presented an efficient implementation of the proper (*in vivo*) outlet boundary conditions in detailed, 3D and time-periodic, simulations of blood flow through arteries. The outlet boundary conditions were obtained from a 1D approximate model based on the Womersley pulsatile flow solution for a viscous fluid through elastic vessels. This approach was applied in a series of 3D and time periodic simulations using the commercial software FLUENT$^{\text{TM}}$, through an asymmetric arterial bifurcation which, however, assumed rigid wall boundary conditions. The present work corrects for this inconsistency by suitably modifying the predictions from the elastic wall 1D solutions as applied as outlet conditions to 3D rigid wall simulations. The modification does not include any adjustable parameters and can be applied to arterial flow problems involving multiple flow outlets. The approach is illustrated here in three cases: a single elastic vessel, the left main coronary arterial bifurcation (that was also examined in the previous publication) and a new, more complex, abdominal aorta case, involving, one, two and multiple flow outlets, respectively. It is shown that the efficiency of the approach is retained even in the presence of the wall elasticity correction. Furthermore, the presence of the elasticity correction leads to results that are more physical with the 3D simulations predictions deviating less from the 1D approximation. Thus, a significant improvement over the previous analysis is achieved.

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Topography-Induced Thickness Variation of Viscoelastic Film

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Two-dimensional, steady flow of a viscoelastic film over topography is studied. This type of flow is encountered in coating flows in the electronics industry. The exponential Phan-Thien and Tanner (ePTT) is used [1], as a viscoelastic constitutive model. The conservation equations along with the constitutive equation are solved via the mixed finite element method combined with a quasi-elliptic grid generation scheme in order to capture the large deformations of the free surface [2]. To solve up to high values of fluid elasticity, represented by De, the constitutive equation is weighted using the SUPG method [3] and the polymeric stress is split following the EVSS-G technique [4]. Moreover, local mesh refinement is performed around the convex corners of the substrate [5]. It is found that the magnitude of the capillary ridge in the film before the entrance to a step down of the substrate and of the capillary depression before a step up is decreased as De increases up to ~0.7 due to increased fluid elasticity. Above this value they increase, because increasing De increases also the shear and elongational thinning of the material, which eventually affect them more. Shear thinning induces higher relative viscosities at the concave corners which locally smooth out the film and, this, in turn, requires a larger ridge to drive the flow through a capillary-generated pressure difference. Increasing the ratio of solvent viscosity over the total (solvent and polymer) viscosity, monotonically increases the magnitude of both the capillary ridge and depression, because the contribution of the constant viscosity solvent to the stress singularity increases proportionally to β. Furthermore, large amounts of inertia can cause the formation of a ridge just after the step up similar to the one observed in Newtonian liquids.

[1]. N. Phan-Thien, R.I. Tanner, J. Non-Newt. Fluid Mech. 2 (1977) 353-365.
[2]. Y. Dimakopoulos, J. Tsamopoulos, J. Comp. Phys. 192 (2003) 494-522.
[3]. A.N. Brooks, T.J.R. Hughes, Comp. Methods Appl. Mech. Eng. 32 (1982) 199-259.
[4]. R.A. Brown, M.J. Szady, P.J. Northey, R.C. Armstrong, Theor. Comp. Fluid Dyn. 5 (1993) 77-106.
[5]. N. Chatzidai, A. Giannousakis, Y. Dimakopoulos, J. Tsamopoulos, J. Comp. Phys. 228 (2009) 1980-2011.

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Perturbation Solutions of Weakly Compressible, Newtonian Poiseuille Flows with Slip along the Wall

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We consider both the planar and axisymmetric Poiseuille flow of a weakly compressible Newtonian fluid assuming that the density obeys a linear equation of state and slip occurs along the wall following Navier's slip equation. A perturbation analysis is performed using the dimensionless isothermal compressibility as the perturbation parameter. Solutions are derived up to the second order and compared with available analytical results. The combined effects of compressibility, slip and inertia are discussed.

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Squeezing of a Finite Amount of Viscoplastic Material Exhibiting Thixotropy

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The flow and shape evolution during the compression of a finite amount of a viscoplastic material exhibiting thixotropic effects is investigated by means of numerical simulations. The problem relates to the popular compression test used for the rheological characterization of non-Newtonian fluids. The flow is modelled in Lagrangian coordinates using the Papanastasiou regularization for the Bingham plastic and a mixed-Galerkin finite element method. Simulations have been performed for compression under both constant load and constant velocity. Results for various Reynolds and Bingham numbers are presented and discussed.

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Deformation of a Bubble in a Viscoelastic Liquid Subjected to Axisymmetric Extensional Flow

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Pressure sensitive adhesives, which are widely used today, are made of tri-block copolymers (polystyrene-polyisoprene or polyacrylates). A common test to characterize their adhesion properties is to place them between two parallel plates and measure the force required to separate them as a function of time. During this test they undergo deformations and, almost always, cavities appear in their bulk or on their interfaces with the substrates. The cavities have been observed to expand primarily in the axial direction leading to fibrillating structures and finally to failure of the material. We will present our simulations of axisymmetric extensional flow of a viscoelastic liquid that contains an initially spherical bubble. The polymer is located between two parallel and coaxial disks, and the cylindrical outer surface is surrounded by air. The flow is induced by the motion of the upper disk under constant velocity, while the lower disk remains stationary. The rheology of the liquid is described by the exponential Phan-Thien Tanner viscoelastic model [1]. We used the mixed finite element Galerkin method combined with a quasi-elliptic transformation (Dimakopoulos & Tsamopoulos [2]) which has been more recently advanced further by incorporating domain decomposition [3]. In this way, deformations of the physical domain much larger that those reported in our previous studies [4] have been computed accurately. The EVSS-G (Elastic Viscous Stress Splitting – G) technique is used to separate the elastic and viscous contributions to the stress tensor together with an SUPG (Streamline Upwind Petrov-Galerkin) discretization of the constitutive equation [5]. Time integration has been carried out with the implicit Euler or the Crank-Nicolson methods. The evolution of the filament and bubble free surfaces depends on the interplay of the viscous, elastic and capillary forces. It was found the when the ratio of the elastic and the capillary forces is small compared to the viscous ones the bubble attains very large deformations. Moreover increasing the *De* number decreases the force at the surface of the upper disk due to extensional thinning, while under the same conditions the stresses develop later.

[1] N. Phan-Thien, R.I. Tanner, J. Non-Newton. Fluid Mech. 2 (1977) 353–365.
[2] Y. Dimakopoulos, J. Tsamopoulos, J. Comp. Phys., 192 (2003) 494-522.
[3] N. Chatzidai, A. Giannousakis, Y. Dimakopoulos, J. Tsamopoulos, J. Comp. Phys. 228 (2009) 1980–2011.
[4] K. Foteinopoulou, Mavrantzas, V., Dimakopoulos, Y. & Tsamopoulos, J., Phys. Fluids, 18, 042106, 1-24 (2006).
[5] M.J. Szady, T.R. Salamon, A.W. Liu, D.E. Bornside, R.C. Armstrong, R.A. Brown, J. Non-Newton. Fluid Mech., 59 (1995) 215.

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Collapse Transitions in Alternating Blocky Copolymers: A Monte Carlo Study

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Alternating blocky copolymers exhibit a rich transition behavior in selective solvents, which has implications in life sciences and applications to the design and material selection of thermo and pH-sensitive materials and membranes. We have studied the transitions of such systems via Monte Carlo simulations. Copolymers of the type $(AAA\ldots)_{n1}(BBB\ldots)_{n2}(AAA\ldots)_{n1}(BBB\ldots)_{n2}\ldots$ with blocks A and B chemically connected were simulated. Our results demonstrated that the most important factor, which controls block copolymer response to external stimuli, is their chemical composition. We focused on the extreme case of a single polymer chain of N = 1000 units, distributed in alternate blocks of $n_1 = n_2 = 100$ units (A- and B- blocks). The solvent was quite selective, i.e. A-blocks (500 units) were soluble $E_{AA} = 0.10kT$ (good solvent, almost athermal) whereas, the B-blocks (500 units) were quite insoluble $E_{BB} = 0.45$ (poor solvent). In this case an extended critical region was observed, characterized by the presence of several distinct intermediate states between coil and globules, and by fluctuations strong enough to induce spontaneous transitions between these states. Our findings, which are supported by experimental data, underline that, even in a case of very high blockiness, the alternating architecture introduces qualitatively new phenomena.

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Structure and Dynamics of Non-Equilibrium Polymer Melts through Hierarchical Multi-Scale Dynamic Simulations

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Molecular simulations are a very useful tool for the study of polymeric material. Here we present results concerning polymers, under equilibrium and non-equilibrium conditions, through such a hierarchical multi-scale simulation approach. The proposed methodology consists of two stages [1-3].The first one involves state-of-the-art atomistic molecular dynamics (MD) simulations of small systems. In the second stage a CG model for the polymer chain is developed using static and dynamic information from the atomistic simulations. With this systematic approach structure and dynamics of polymer can be quantitatively predicted through the CG simulations and directly compared to experimental [3]. As a test case polystyrene (PS) melts are examined.

Furthermore, non-equilibrium polymeric liquids (PS) under shear flow are examined by performing atomistic and CG non-equilibrium MD (NEMD) simulations [4]. We present results about both structural (chain conformation and pair distribution function) and dynamical (relaxation time and diffusion coefficient) properties as a function of the shear rate. We found that the large-scale chain conformation is reasonably well predicted by the CG model up to an intermediate flow strength (Weissenberg number $Wi<10$), beyond which, however, a significant discrepancy between the atomistic and the CG models is developed.

1. *"Simulation Methods for Polymers"* ed. Theodorou, D. N., Kotelyanski, M., (Marcel Dekker: New York, 2004).
2. V. Harmandaris et al. *Macromolecules* **36**, 1376 (2003); *Macromolecules* **39**, 6708 (2006); *Macrom. Chem. and Physics*, **208**, 2109 (2007).
3. V. Harmandaris and K. Kremer *Macromolecules* **42**, 791 (2009); *Soft Matter* **5**, 3920 (2009).
4. C. Baig and V. Harmandaris *Macromolecules* **43**, 3156 (2010).

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Primitive Path Dynamics and Contour Length Fluctuations in Entangled Polymer Melts: A Molecular Simulation Study

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The dynamical and rheological behavior of long-chain polymers are well described, qualitatively and quantitatively, by the reptation model. Each chain is represented by the axis of an enclosing tube, named the Primitive Path (PP), and is supposed to relax by performing one-dimensional curvilinear diffusion along the enclosing tube. The latter represents topological constraints imposed by surrounding chains, which hinder 3D motion. Additional relaxation mechanisms, such as contour length fluctuations (CLF) and constraint release (CR), have been proposed as necessary mechanisms for improving agreement of theory with experimental findings.

In this work, we will present a combined topological and dynamical simulation study of CLF and CR in polymer melts. Linear Polyethylene and a set of coarse-grained polymer melts of increasing chain length, N, will be examined. Our analysis is based on Molecular and Dissipative Particle Dynamics (DPD) trajectories (of united atom PE and coarse-grained model systems, correspondingly), reduced to the level of PPs by the CReTA algorithm.

At first, we will discuss the onset of tube confinement, as extracted from the mean square displacement (MSD) of the central monomers of melt chains. From the MSD plots we will also identify the characteristic time scales predicted by reptation theory. By defining appropriate MSDs for the PPs we will show how these time scales appear at the level of PPs, and also how CLF and CR force PPs to escape their confining tubes faster than the parent melt chains. Furthermore, by analyzing PP contour length fluctuations we will show that the characteristic time scale for CLF is the Rouse time, τR, which scales with chain length N as N^2, as predicted by reptation theory. Additional results show that the shortest paths constructed by the CReTA algorithm are reliable ***dynamical*** representations of the PPs invoked by tube theory.

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Molecular Modeling of Cavitation in Polymer Melts and Rubbers

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Cavitation in polymer melts and rubbers is of great technological significance. It can be described as a phase separation phenomenon, wherein a *cavity* develops within a condensed phase that is being subjected to an isotropic stress. Below a certain negative pressure, the dense polymer phase becomes unstable. From thermodynamic considerations, the stress at the *limit of stability* is higher than experimental observations. On the other hand, a *continuum mechanics* analysis of heterogeneous nucleation predicts that a preexisting cavity in a neo-Hookean material will grow without limit when the hydrostatic pressure is more tensile than the Young's modulus, in approximate agreement with experimental observations.

A molecular-level understanding of cavitation in amorphous polymers upon imposition of mechanical stress is still lacking. Molecular Dynamics simulations of crosslinked amorphous Polyethylene (PE) and of linear PE melts were conducted in order to study cavitation as a function of prevailing stress and molecular characteristics and to understand its dependence on cohesive interactions and entropy elasticity of the chains.

We found that homogeneous crosslinked and linear PE melts, in the absence of flaws, cavitate at their limit of stability, where the stress is on the order of 50MPa, and therefore much higher than the Young's modulus of the system. At this stress level, cohesive interactions in the polymer are overcome. For crosslinked PE there is a slight dependence of cavitation stress on crosslink density, and for linear melts on chain length. The presence of pre-existing flaws decreases the estimated cavitation stress.

By loading or unloading, that is, by applying an increasing or decreasing hydrostatic tension starting from a homogeneous or cavitated initial state, correspondingly, two branches, in the form of a hysteresis loop, are obtained in the P-V diagram of the rubber. The higher-volume branch leads to closure of a preexisting cavity at a hydrostatic tension that is lower than the tension at the limit of stability of the homogeneous polymer, and comparable to the Young's modulus of the rubber. This critical level of stress, below which a cavity cannot survive in the material, appears to be intimately related to the entropy elasticity of the chains.

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Effective Interaction between Diblock-Arm Star Copolymers: A Molecular Dynamics Study

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Amphiphilic star copolymers (stars with di-block arms, A-type and B-type) are interesting polymeric materials with a number of potential applications. In this work, Molecular Dynamics simulations have been carried out in order to extract the effective interaction, in terms of a pair potential, between two star-polymers consist of di-block arms. We study systems consist of two star polymers for a number of different functionalities (*f*). Star arms comprise of two types of beads with lengths *n1* and *n2* and we examine different length ratios (*n1/n2*). The inner beads realize poor solvent conditions while the outer beads are under good solvent conditions. This study leads to a phase diagram of the star size (*f*) versus the relative ratio of the lengths of the attractive over the repulsive part of the arms (*n1/n2*) which classifies systems of stars as stable or unstable and provides important information for the polydispersity of the corresponding solutions.

The potential extracted from this study will be a suitable effective potential for the interaction between diblock arm star polymers and can be used in a coarse grained model of a solution of these stars, in order to examine structural and dynamical properties.

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Micro-Structure and Particle Dynamics in Suspensions of Size-Dispersed Colloids

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We present a simulation study of structural and dynamic properties of polydisperse systems of soft spheres that interact via power-law potentials with a varying degree of "softness". Comparisons were made for crystal and amorphous phases at their coexistence points. It is shown, through structural analysis, that as potential interactions soften the "quality of crystallinity" of both monodisperse and polydisperse systems deteriorates. In general, polydisperse crystalline phases are characterized by a more ordered structure than the corresponding monodisperse ones (i.e. for the same potential softness). This counter-intuitive feature draws its cause mainly from the fact that the coexistence pressure is much higher for polydisperse systems. The trend diminishes for softer potentials. Potential softness eventually produces substitutionally disordered crystals. However, substitutional order is apparent for the hardest potential interactions. Diffusion-wise crystals appear quite robust with a slight difference in the vibrational amplitudes of small and large particles. This difference diminishes with potential softness.

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Rouse Theory for Polymer Rings and Comparison with Atomistic Molecular-Dynamics Simulations

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Recently, careful experimental measurements [1] have shown that the rheological response of a polystyrene ring melt contaminated with linear chains can differ significantly from that of the corresponding pure ring system. Motivated by this, we have conducted recently atomistic molecular dynamic simulations of model ring polyethylene (PE) melts, ranging in molecular length from N=24 up to N=400 carbon atoms per molecule [2]. This has allowed us to study in detail their conformational and viscoleastic properties and how these compare with those of linear PE melts of the same chain length (the linear analogues) and reported theoretical [3] and experimental findings [4]. We have also derived the Rouse theory for polymer rings (elements of which have already appeared in the literature; see, e.g., [3]) to its entirety. The Rouse theory is found to provide a satisfactory description of the simulation findings, even for chain lengths up to C_{400}. In agreement with previous experimental studies [5], our simulations support that unentangled polymer rings exhibit a faster dynamics and a lower viscosity than linear analogues.

[1] M. Kapnistos, M. Lang, D. Vlassopoulos, W. Pyckhout-Hintzen, D. Richter, D. Cho, T. Chang, M. Rubinstein, *Nature Materials* **7**, 997 (2008).
[2] G. Tsolou, N. Stratikis, C. Baig, P.S. Stephanou, V.G. Mavrantzas, *Macromolecules* **43**, 10692 (2010).
[3] B.H. Zimm, W.H. Stockmayer, *J. Chem. Phys.* **17**, 1301 (1949); H. Watanabe, T. Inoue and Y. Matsumiya, *Macromolecules* **39**, 5419 (2006).
[4] V.S. Arrighi, S. Gagliardi, A.C. Dagger, J.A. Semlyen, J.S. Higgins, M.J Shenton, *Macromolecules* **37**, 8057 (2004).
[5] J. Roovers, *Macromolecules* **21**, 1517 (1988).

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Quantifying Chain Reptation in Entangled Polymer Melts: Topological and Dynamical Mapping of Atomistic Simulation Results onto the Tube Model

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According to the tube model [1,2], topological interactions that dominate dynamics in entangled polymer melts can be captured by considering a mean-field tube around the chain as it moves in the sea of the rest of the chains. The tube diameter is then controlling the strength of the topological interactions. We present a systematic methodology [3] which allows one to calculate the segment-survival probability function $\psi(s,t)$ describing the probability that at a time t, a segment s along the primitive path is still inside the initial (defined at t=0) tube, directly from trajectories accumulated in the course of long molecular dynamics simulations. The computed $\psi(s,t)$ curves account directly for reptation, chain local transverse fluctuations driven mainly from constraint release (CR) and regeneration mechanisms, and contour length fluctuations (CLFs). The CLF and CR mechanisms have been shown to facilitate relaxation in monodisperse melts, causing significant effects on the rheological properties [4]. The CR mechanism is particularly important in bidisperse melts when the surrounding matrix chains are shorter than the probe chains [5]. Linear viscoelastic properties, such as the zero shear rate viscosity and the spectra of storage and loss moduli, obtained on the basis of the computed $\psi(s,t)$ curves for three different polymer melts (polyethylene, *cis*-1,4-polybutadiene and *trans*-1,4-polybutadiene) are seen to be consistent with experimental rheological data.

[1] de Gennes, P.G., *J. Chem. Phys*., **55**, 572 (1971).
[2] M. Doi, S.F. Edwards, *J. Chem. Soc. Faraday Trans. 2*, **74**, 1789 (1978); M. Doi, S.F. Edwards, *The Theory of Polymer Dynamics* (Clarendon Press, Oxford, 1986).
[3] P.S. Stephanou, C. Baig, G. Tsolou, V.G. Mavrantzas, M. Kröger, *J. Chem. Phys.* **132**, 124904 (2010).
[4] P.S. Stephanou, B. Chunggi, G. Tsolou, V.G. Mavrantzas, *Soft Matter* DOI:10.1039/C0SM00327A (2010).
[5] Baig, C., P.S. Stephanou, G. Tsolou, V.G. Mavrantzas, *Macromolecules* **43**, 8239 (2010).

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POSTER CONTRIBUTIONS

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