The National IOR Centre of Norway

Description of the Rheological Properties of Complex Fluids Based on the Kinetic Theory

Project 1.3.4

Project managers: Prof. Aksel Hiorth and postdoc Dmitry Shogin
PhD students and postdocs: postdoc Dmitry Shogin
Other key personnel: Prof. Per Amund Amundsen, Prof. Merete Vadla Madland
Project duration: 01.07.2015–30.06.2018

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Final Project Report

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Project number and location (UiS, NORCE, IFE): PR-10373-08 / UiS with part of the work conducted at NORCE laboratory
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1. Executive summary

Primary objective:
Investigate how microscopic physics-based differential tensor models of polymeric liquids can be applied to describe, explain, and predict non-Newtonian phenomena in complex flows relevant for improved oil recovery applications and prepare a background for creating a lattice Boltzmann numerical solver capable of tackling the constitutive equations of such fluid models.

Secondary objectives:
(A) Based on advanced thermodynamics, develop an extended fluid model for polyelectrolyte solutions from first principles to understand and predict the impact of solvent salinity on non-Newtonian flows of salt-sensitive polymer solutions.
(B) Use the realistic equations of non-Newtonian fluid dynamics to obtain analytical expressions for the material functions of different polymer fluid models and analytical solutions for simple flows of fluids described by such models.
(C) Compare theoretical predictions of physically realistic polymer fluid models with rheological measurements and calibrate the models to experimental data.

Polymeric liquids—liquids consisting of long molecules or containing them—are of essential importance to modern technology. Their area of application includes production of plastics and gels, cosmetics, food industry, biological physics, and improved oil recovery (IOR) procedures.

Physically realistic modelling of polymeric flows is not possible without understanding the underlying microscopic mechanisms. It is especially important for IOR applications, where complex flows of polymer solutions through porous media are involved. Incorporation of realistic polymer models into a reservoir simulation tool will help to choose the right polymer for injection by predicting the result of this operation. Correct predictions shall reduce the cost of operation and lower the negative impact on the environment.

Polymeric liquids do not obey the laws of classical, or Newtonian, fluid dynamics. The qualitative difference between Newtonian and non-Newtonian fluid behaviour is drastic: non-Newtonian fluids can become locally anisotropic when they flow. These properties of polymeric liquids are encoded in the stress tensor, which is coupled to the flow pattern in a non-trivial way. This coupling is described

by the tensor constitutive equations, derived from molecular transport theory.

For over 70 years, the tensor nature of the constitutive equations has mostly been overlooked in applications. In practice, one often relies upon ad hoc non-Newtonian fluid descriptions, e. g. the power-law and the Carreau-Yasuda fluid models. These "generalized Newtonian" fluid models describe the non-Newtonian character of polymeric fluids by a local viscosity that is a function of the velocity gradient. Such simple models are restricted to steady-state shear flows and, therefore, are not capable of describing the flow phenomena in complex geometries (like porous media) and in time-dependent flows. This makes predictions based on such models unreliable. Moreover, realistic non-Newtonian fluid models, respecting the anisotropic properties of polymeric liquids, are presently not implemented even in high-end computational program packages like COMSOL Multiphysics.

This project aims at investigation, utilization, calibration, and further development of nonlinear differential non-Newtonian fluid models having basis in non-equilibrium thermodynamics, in particular, the FENE-P dumbbell and bead-spring-chain models for dilute polymer solutions and the Phan-Thien–Tanner (PTT) models for concentrated polymer solutions and polymer melts. In these models, the fluid description is first obtained at molecular scales, and then extended by means of statistical physics to hydrodynamical scales: The constitutive equations for the stress tensor are formulated. Thus, the material functions of the fluid, such as the non-Newtonian viscosity, are not prescribed a priori, but obtained from the constitutive equations. The equations of fluid motion, together with the constitutive equations, can in principle be solved for any flow geometry, provided that the hydrodynamic description of the fluid applies. The effective flow parameters, such as apparent viscosity and apparent shear rate, can then be determined from these solutions.

2. Introduction and background

Polymer solutions contain macromolecules and therefore possess very specific properties. Unlike oil or water, obeying the laws of classical, or Newtonian, fluid dynamics, macromolecular fluids do not obey these laws: They are non-Newtonian. To predict the motion of any fluid, one needs to solve the equations of fluid dynamics, known as the (generalized) Navier-Stokes equations. One of the key physical quantities included in these equations is the stress tensor that describes how forces are distributed inside the fluid.
For Newtonian fluids, the stress tensor is of simple form and can be calculated provided the the viscosity of the fluid is known. For non-Newtonian fluids, it is more difficult to evaluate the stress tensor. It can be found from a so-called constitutive equation, which in turn must be derived by means of non-equilibrium thermodynamics.

The attempts to model polymeric flows without using the stress tensor are based on correlations for non-Newtonian fluid properties obtained from laboratory experiments. However, these correlations are only valid at conditions at which they are measured. In contrast, the conditions in the reservoir are highly varied, which implies large ranges of pressures, temperatures, salt concentrations, and pore geometries. This makes correlation-based polymeric flow modelling unreliable.

Solving the equations of fluid dynamics together with a tensor constitutive equation using a modern computational program package, like COMSOL Multiphysics, could be another viable option. However, such programs currently support modelling non-Newtonian flows only by using so-called "generalized Newtonian" constitutive equations (which means that local viscosity is an apriori known function of the velocity gradient tensor). Such non-Newtonian fluid models are only applicable to steady flows in

very simple geometries (known as simple shearing flows). In the reservoir, the polymeric liquid flows through a porous rock, which is an example of rather complex geometry, and the flow is typically time-dependent. Hence, the currently available commercial packages cannot be effectively used in modelling polymer IOR procedures.

Thus, realistic modelling of polymeric flows must involve understanding the nature of macromolecular fluids, derivation of the constitutive equations based on microscopic physics, and solving these equations together with the equations of fluid motion. Development of such methods will drastically increase the predictive power of engineering calculations, allowing to spare time and resources spent in the laboratory, together with increasing the efficiency of IOR procedures.

The focus of this project is implementation and extension of the advanced non-Newtonian fluid models having basis in non-equilibrium thermodynamics. These models lead to nonlinear differential constitutive equations for the stress tensor of the fluid. Examples of such non-Newtonian fluid models are the FENE-P dumbbell/bead-spring-chain models for dilute polymer solutions and the Phan-Thien–Tanner models for concentrated solutions and polymer melts.

Although the behaviour of non-Newtonian fluids is very specific and strongly depends on the kind of flow, the constitutive equations contain a limited number of constant parameters. These parameters can be determined by relatively simple rheological experiments. Then, solving the equations of fluid motion together with the constitutive equations will predict the dynamics of the fluid in any kind of flow. The effective flow parameters of practical interest (such as apparent viscosity and apparent shear rate), can be determined from such solutions.

Flows of polymeric liquids described by differential tensor fluid models have been simulated numerically with some success. However, the progress in this direction has been slow. This project, inter alia, aims at preparing a background for creating a lattice Boltzmann numerical solver capable of tackling the constitutive equations of such fluid models.

3. Results (sorted according to Secondary objectives)

(A-I) A new differential non-Newtonian fluid model describing dilute solutions of salt-sensitive polymers (polyelectrolytes)—Charged FENE-P (C-FENE-P) dumbbell model—has been constructed, and its rheological properties in simple flows (steady shear flow, steady uniaxial and biaxial extension, small-amplitude oscillatory shear, and start-up and cessation of steady shear flow) have been investigated [5].

(A-II) The rigid dumbbell (RDB) model, which might be useful for rheological characterization of dilute solutions of stiff biopolymers, has been recovered as the limiting case of the C-FENE-P dumbbell model.

(B-I) Exact analytical description of simple shear flows of polymer solutions through pipes, slits, grids, and capillary bundles have been obtained using the framework of the FENE-P dumbbell non-Newtonian fluid model [1, 2, D4–D6].

(B-II) Exact analytical solutions for different kinds of rotational and helical flows of FENE-P dumbbells, linear and exponential Phan-Thien–Tanner fluids have been obtained. In particular, descriptions of the Weissenberg effect (rod climbing) has been obtained for these fluid models.

(C-I) Non-Newtonian viscosity of solutions of EOR polymers (including partially hydrolyzed polyacrylamides, Xanthan gum, and hydroxyethylcellulose) has been investigated experimentally at different concentrations and compared to predictions of tensor non-Newtonian fluid models. [4, D7]

(C-II) The relation between the Non-Newtonian viscosity and the first normal stress coefficient of different EOR polymers has been studied experimentally and tested against the predictions of the physical polymer fluid models. For some polymers, useful correlations were established. [3, D7]

(C-III) The practical limits of applicability of the FENE-P dumbbell and exponential Phan-Thien–Tanner non-Newtonian fluid models to describe the non-Newtonian viscosity of IOR polymers were established. [4, D7]

(C-IV) It was established experimentally which polymer solutions can be considered dilute in terms of linearity of non-Newtonian viscosity in concentration. [4, D7]

(C-V) It was shown that the impact of molecular weight on the non-Newtonian viscosity of polymers is (at the very least, qualitatively correctly) described by the FENE-P bead-spring-chain polymer model. It was demonstrated that the impact of concentration in the dilute region is accurately described by the kinetic theory-based polymer fluid models. [4]

(C-VI) The impact of salinity on the non-Newtonian viscosity of salt-sensitive EOR polymers has been investigated experimentally. The results were shown to be in qualitative agreement with the new C-FENE-P dumbbell polymer model [6].

(C-VII) Based on the experimental results obtained at NORCE, a procedure allowing to relate the effective charge parameter of the C-FENE-P dumbbell model to the actual salt concentration in the solution has been proposed.

4. Conclusion

Physics-based models of polymeric liquids (the FENE-P dumbbell model and its modifications and the Phan-Thien–Tanner models) predict a wide range of non-Newtonian flow phenomena and thus are shown to be a promising tool for rheological characterization of EOR polymer solutions and modelling complex and time-dependent polymer flows [3–6, D1, D2, D7]. Still, because of mathematical complexity of the underlying equations, practical implementation of these models in numerical solver codes is a challenge to be resolved in the future work.

From 01.07.2018, the project proceeds to Phase II, funded by VISTA (VISTA project 6370).

5. Future work/plans

(a) Finalize and publish the paper on the C-FENE-P dumbbell model and its rheological properties.

(b) Investigate experimentally the transient rheological behavior of EOR polymer solutions (small-amplitude oscillatory shearing, start-up and cessation of steady shear flows) and find out how it is influenced by the salinity of the solvent.

(c) Check the opportunity to model mechanical degradation of polymer solutions using a physical

polymer fluid model that directly accounts for the length of the polymeric chains (e.g., the FENE-P bead-spring-chain model)

(d) Obtain exact analytical descriptions of rheological properties of Phan-Thien–Tanner fluid models in simple transient flows of rheological interest.

(e) Co-supervise (within UiS/NORCE collaboration) a PhD project aiming at developing a numerical solver code capable of solving the physically realistic equations of non-Newtonian fluid dynamics for complex and time-dependent flows using the lattice Boltzmann method. Use these results to construct effective engineering theories for flows through porous media and study how oil distribution in the pores is changed when two phases, oil and polymer, are present.

6. Dissemination of results (in chronological order)

[D1] D. Shogin, *The kinetic theory approach to the rheology of polymer solutions,* oral presentation. Lunch & Learn Seminar, University of Stavanger, Norway (2016)

[D2] D. Shogin, *Explaining and modelling the rheology of polymeric fluids with the kinetic theory,* oral presentation. IOR Norway 2016 Conference Workshop, Stavanger, Norway (2016)

[D3] D. Shogin, *Explaining and modelling the rheology of polymeric fluids with the kinetic theory,* oral presentation. Visit from DTU Danmark, University of Stavanger, Norway (2016)

[D4] D. Shogin, *The FENE-P model of polymeric liquids: Analytical solutions for Poiseuille flow and flow in a capillary bundle,* oral presentation. Lunch & Learn Seminar, University of Stavanger, Norway (2017)

[D5] D. Shogin, P. A. Amundsen, A. Hiorth, and M. V. Madland, *Rheology of polymeric flows in circular pipes, slits, and capillary bundles: Analytical solutions from kinetic theory,* poster presentation. 19th European Symposium on Improved Oil Recovery / IOR Norway 2017, University of Stavanger, Norway (2017)

[D6] D. Shogin, P. A. Amundsen, A. Hiorth, and M. V. Madland, *Modelling the rheology of two-phase polymer flow,* poster presentation. 19th European Symposium on Improved Oil Recovery / IOR Norway 2017, University of Stavanger, Norway (2017)

[D7] D. Shogin, A. Lozhkina and M. Lutskina, *Describing IOR polymer solutions with differential tensor non-Newtonian fluid models,* poster presentation. IOR Norway 2018, Stavanger, Norway (2018)

7. References (in chronological order)

[1] D. Shogin, P. A. Amundsen, A. Hiorth and M. V. Madland, *Rheology of polymeric flows in circular pipes, slits, and capillary bundles: analytical solutions from kinetic theory*, proceedings of 19th European Symposium on Improved Oil Recovery / IOR Norway 2017 (2017)

[2] D. Shogin, P. A. Amundsen, A. Hiorth and M. V. Madland, *Modelling the rheology of two-phase polymer flow*, proceedings of 19th European Symposium on Improved Oil Recovery / IOR Norway 2017 (2017)

[3] A. Lozhkina, *Understanding shear flow material functions of IOR polymers.* MS Thesis, University of

Stavanger, Supervisor D. Shogin (2018)

[4] M. Lutskina, *Describing viscosity of IOR polymer solutions with differential non-Newtonian fluid models.* MS Thesis, University of Stavanger, Supervisor D. Shogin (2018)

[5] C. Orioma, *Charged FENE-P non-Newtonian fluid model.* MS Thesis, University of Stavanger, Supervisor D. Shogin (2018)

[6] V. Stanislavskiy, *Investigating the impact of solvent salinity on the viscometric functions of IOR polymers.* MS Thesis, University of Stavanger, Supervisor D. Shogin (2018)