**Constitutive equations for unentangled polymer melts guided by principles of non-equilibrium thermodynamics**

Based on principles of non-equilibrium thermodynamics, we derived a generalized constitutive model for polymer melts which incorporate terms that account for anisotropic hydrodynamic drag in the form suggested by Giesekus, finite chain extensibility with non-linear molecular stretching, non-affine deformation, and variation of the longest chain relaxation time with chain conformation. In the new equations (one evolution equation for the conformation tensor and one relating the stress tensor with the conformation tensor), the expression for the Helmholtz free energy of deformation is defined such that the entropy remains bounded even at high deformation rates, as it should from a physical point of view. Key elements in the new constitutive model are the functions describing the dependence of the non-equilibrium free energy and relaxation matrix on the conformation tensor. Restrictions on the parameters entering these two functions have been obtained by analyzing the thermodynamic admissibility of the model. With suitable choices of these two functions, the new set of equations reduces to many well-known viscoelastic models. The new equations are used to describe (fit) rheological data provided either by experimental measurements on industrial samples [P. S. Stephanou, C. Baig, V.G. Mavrantzas, and J. Den Doelder, (2011) (report)] or obtained through Non-Equilibrium Molecular Dynamics (NEMD) simulations in shear and planar elongation (see Fig.). More recently, we have also elaborated on the use of a variable non-affine or slip parameter.

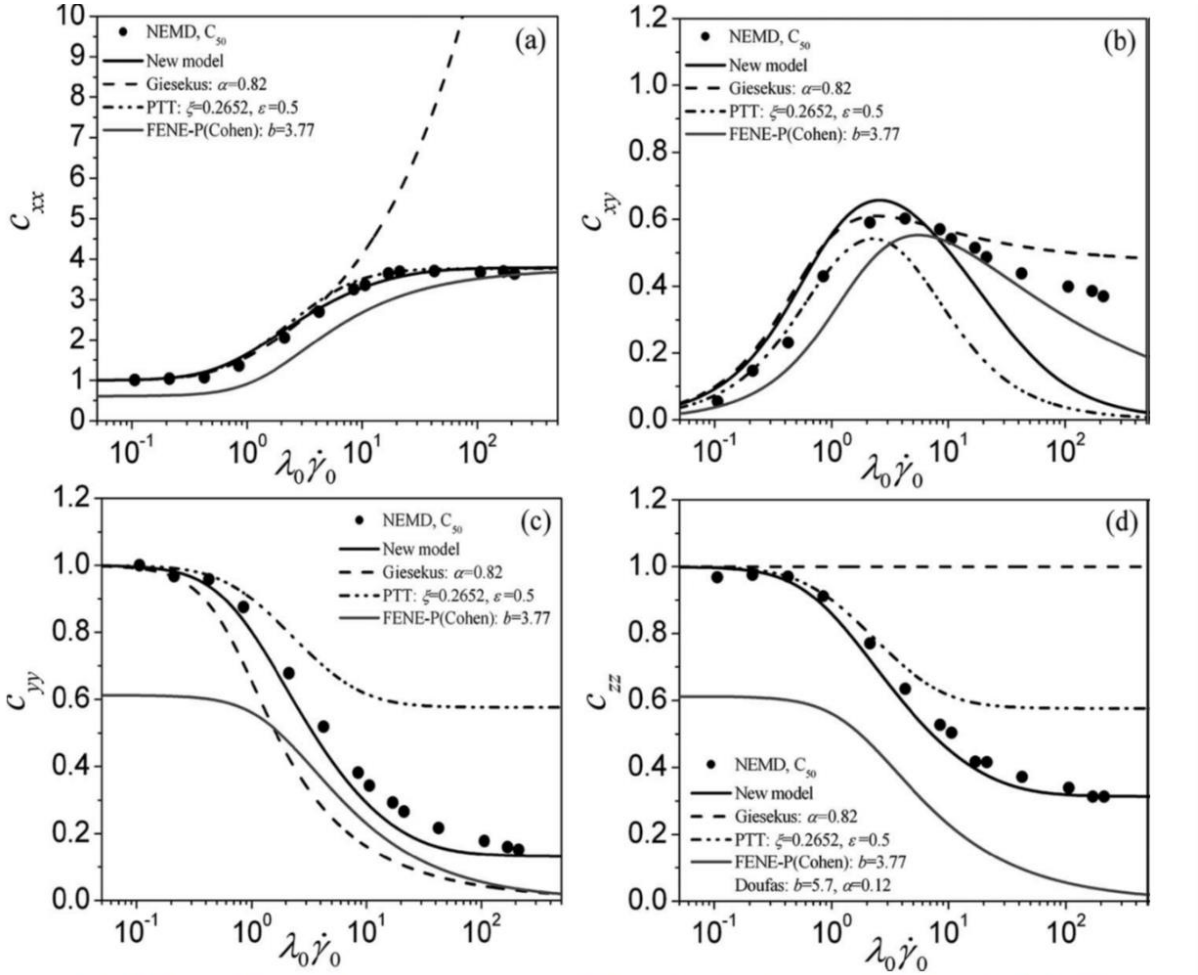


*Fig.: Model predictions for the nonzero components of the conformation tensor in steady shear for the $C_{50}H_{102}$ polyethylene melt along with comparison with the NEMD simulation results and the predictions of other models based on best fits*

**Reference**


1. P. S. Stephanou, C. Baig, V.G. Mavrantzas, *J. Rheol.* 53, 309-337 **(2009).**

2. V. M. Nikiforidis, D. G. Tsalikis**,** and **P. S. Stephanou***, "On the use of a non-constant non-affine or slip parameter in polymer rheology constitutive modeling", *Dynamics*, 2, 380–398 **(2022)** [invited, free-of charge, Selected for Cover page]