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# Non-linear stress-orientation behavior of flexible chain polymers under fast elongational flow

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ABSTRACT

Closed-form analytical formulas are proposed for non-linear stress-orientation relation valid in the entire range of tensile stresses, intermediate and high, basing on the inverse Langevin chain statistics. Tensile force and orientation characteristics for single, flexible chain macromolecule are reconsidered in a closed-form Padè approximation of the inverse Langevin function in the entire range of chain extensions, as well as the dynamics of molecular deformation and orientation for systems of chains subjected to uniaxial elongational flow. Average stress and orientation tensors, not collinear in the non-linear range, as well as the tensile stress and axial orientation factor of the chain segments in the system are calculated. For the intermediate tensile stresses, the closed-form formula is derived in the first non-Gaussian term approximation of the inverse Langevin function with the assumption of dominating longitudinal elongation of the chains. The high-stress non-linearity formula is derived with the Padè and Peterlin modulus approximations and aligned chain end-to-end vectors by the flow. Both formulas are validated by exact numerical calculations without the assumptions and influence of the approximations is estimated. Ranges of applicability of the formulas are illustrated and examples of their application are presented.

## 1. Introduction

Molecular orientation is one of the most important structural characteristics strongly influencing dynamics of polymer processing and mechanical properties, also by the effects of oriented crystallization if present. Usually, the orientation is produced by tensile stresses applied during the processing. In this paper, we focus on molecular orientation in polymer fluids subjected to uniaxial elongational flow. In the fluids (melts, solutions), the orientation is produced during melt or solution spinning of fibers, film blowing, film casting, etc. Structure formation during the processing is controlled by the strain rate, or stress, and orientation of the chain macromolecules results from the competition between the orienting effects of the flow field and disorientation by the Brownian motion.

The relation between tensile stresses and molecular orientation plays key role in the dynamics of polymer processing and structure formation. Extension and orientation of chain macromolecules under the elongational flow results in significant enhancement of tensile modulus and tenacity of the polymer. The uniqueness of the stress-orientation relation in the flexible chain systems in a wide range of tensile stresses has been discussed in [1–4]. Orientation of the chain segments in the amorphous phase is described by the Hermans axial orientation factor [5]. Values of the orientation factor change between zero in relaxed, zero-stress systems and unity in the limit of infinite tensile stresses. The stress-orientation behavior cannot be linear at higher stresses because of

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finite value of the orientation factor at infinite stress. Numerical calculations of the stress-orientation behavior were performed in [1] for uniaxial elongational flow for systems exhibiting Langevin chains statistics and have shown a unique non-linear stress-orientation relation in the entire range of tensile stresses. The approach [1] was based on computations of the stress and orientation factor in the non-linear systems subjected to elongational flow by averaging the values numerically with the chain orientation distribution under the flow with indirect calculation of the inverse Langevin function, without any closed-form analytical formula proposed.

Besides high impact on mechanical properties, molecular orientation influences the thermodynamic properties, accelerates crystallization and rises the equilibrium melting temperature [6–10]. In case of crystallizing polymers, the stress-controlled orientation of amorphous phase plays significant role in the kinetics of orientated crystallization which stabilizes oriented molecular structure and high properties of polymers.

Structure formation mechanisms during polymer processing under fast elongation rates involve fast development of molecular orientation. Under high tensile stress conditions, non-linear effects in the development of amorphous orientation vs. stress and its influence on crystallization kinetics should be accounted in modeling of polymer processing. High elongation rates characteristic for fast melt processing, like high-speed melt spinning or pneumatic melt spinning under fast air jets, result in significant uniaxial extension and orientation of chain macromolecules. Dynamics of the processing and formation of oriented structure of the material are strongly influenced by fast oriented crystallization induced under such condition, in particular for polymers slowly crystallizing in relaxed isotropic conditions. The role of oriented crystallization in the modeling we will discuss in a separate paper.

In this work we focus on modeling of high molecular deformation and orientation of flexible chain polymers under fast uniaxial elongational flow. We propose a closed-form analytical formula for non-linear stress-orientation relation valid in the range of high tensile stresses which accounts for finite chain extensibility in the limit of infinite stresses, as well as a formula valid in the range of low and intermediate stresses above the Gaussian range. The high-stress formula is derived basing on the inverse Langevin chain statistics in the Peterlin [11] and a rounded Padè approximation proposed by Cohen [12], while the low and intermediate-stress formula is based on the first non-Gaussian term approximation of the inverse Langevin function in the chain statistics.

The relation between the applied stress and orientation of the chain segments produced under the stress is a consequence of statistical properties of flexible chain macromolecules. The tensile stresses cause deformation of the chain macromolecules, change distribution of the chain end-to-end vectors, affect the system free energy, and produce uniaxial orientation of the chain segments under the elongational flow. We consider flexible, linear non-Gaussian chains in the modeling. At high elongation rates, applicability of the Gaussian statistics is strongly limited and the inverse Langevin chain statistics is used. In undeformed systems, the equilibrium distribution of the end-to-end vectors of flexible chain macromolecules and free energy of the chains are given by Kuhn and Grün [13]. Uniaxial stretching or uniaxial elongational flow provide highest orientational response to the external stresses [14,15]. The average stress and orientation tensors are obtained by averaging the stress and orientation tensors of individual chains with the time-dependent distribution of the chain end-to end vectors in the system [15–17].

For the purpose of this work, in Section 2 we reconsider the tensile force and segmental orientation of single chain macromolecule in the entire range of chain extension, between zero and full extension, in the closed-form Cohen approximation of the inverse Langevin function [12]. As the base for deriving the closed-form non-linear stress-orientation formulas, in Section 3 we reconsider our earlier results on the dynamics and the average chain elongation coefficients in systems of flexible chains subjected to uniaxial elongational flow in the entire range of tensile stresses, between zero and infinity, as dependent on the elongation rate, flow time and the chain length. Cohen approximation of the chain statistics and the Peterlin modulus [11] and are used for the systems.

## 2. Single chain macromolecule under tensile force

We reconsider the entropic character of tensile forces applied to a single chain, and next to the system of chains subjected to elongational flow. First, we refer to basic formulation of the chain statistics necessary in discussing of the non-linear stress-orientation behavior in this work. The equilibrium distribution of the end-to-end vectors $\boldsymbol{h}$ of linear chains composed of $N$ freely jointed segments in an undeformed systems under quiescent conditions reads [13]

$$W(\mathbf{h}) = Const \cdot \exp[-N \int_0^{h/Na} \mathrm{L}^{-1}(x)dx] \tag{1}$$

where $a$ is the statistical segment length, $h/Na$ characterizes chain extension, $\mathrm{L}^{-1}(x)$ is the inverse Langevin function. The models with the Langevin chain statistics characterize non-linear reduction in the chain entropy and increase in the axial tensile force with increasing the chain extension. The distribution is spherical and changes its symmetry under external forces - uniaxial, biaxial, etc.

The inverse Langevin function cannot be represented in a closed form and an analytical or numerical approximations are required. In the series expansion approximation we have [18]

$$\mathrm{L}^{-1}(x) = 3x + \frac{9}{5}x^3 + \frac{297}{175}x^5 + \frac{1539}{875}x^7 + \frac{126117}{67375}x^9 + \frac{43733439}{21896875}x^{11} + \frac{231321177}{109484375}x^{13} + \frac{20495009043}{1944989921875}x^{15} + \ldots \tag{2}$$

where $0 \le x \le 1$. The higher order terms introduce non-linear corrections to the first Gaussian term. At higher chain extensions, $x = h/Na$, convergence of the series is very week and a growing number of terms is required to maintain reasonable accuracy.

The best easy-to-use closed-form analytical formula for the inverse Langevin function has been proposed by Cohen in the form of rounded {3/2} Padé approximation [12] and is referred to as the Cohen approximation

$$\mathrm{L}^{-1}(x) \cong x\frac{3-x^2}{1-x^2} \tag{3}$$