Viscoelastic properties of linear polymer melts as effect of broken axial symmetry and mutual uncrossability of macromolecules

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Dedicated to the memory of my father F.N. Fatkullin

Abstract

On the basis of the exact Green–Kubo formula for viscosity it is rigorously shown that the zero-shear viscosity of polymer melts is totally determined by the Fixman stress-tensor which represents interchain interactions. The Curtiss–Bird approximation for the Fixman tensor permits one to consider it as a sum of effectively single chain tensors. Considering an arbitrary conformation of a macromolecule as a state with broken axial symmetry, the mean-field part of the Curtiss–Bird stress tensor can be expressed as a sum of two terms. The first term reflects the local geometry of the chain conformation and is proportional to the local curvature of the polymer chain. It is proportional to the effective intramolecular entropic stress-tensor. The second term, which has been never considered before, reflects global properties of the spatial distribution of the probe chain segments and mutual uncrossability of polymer chains. It is proportional to the concentration gradient of the probe chain segments. This term leads to a molecular-mass independent plateau of the relaxation modulus and gives the same molecular mass dependence for the viscosity and the terminal relaxation time in polymer melts with molecular masses large enough. The plateau modulus is derived as $G_N^0 \propto k_B T / (\rho_m \widehat{S}^2(0) b^6)$, where $k_B T$ is the temperature factor, ρ_m is the Kuhn segment number density, $\widehat{S}(0)$ is the collective structure factor of polymer melts in the long wavelength limit, and b is the Kuhn segment length. For the Gaussian thread chain model introduced by Schweizer and Curro, the plateau modulus becomes $G_N^0 \propto k_B T / (\rho_m b^2)^3$. This expression is in qualitative agreement with well-known experimental data.
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1. Introduction

The dynamical properties of polymer liquids were always of central interest in polymer physics. The remarkable achievements obtained during the last decades in this field are expounded in detail in

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