Evaluation of Energetic and Entropic Contributions to the Free Energy of Oriented Polymer Melts

Introduction

Writing constitutive equations for polymeric flows has been one of the major engineering challenges for the past half century. In the mid 1970's, under the premise that the total free energy of the fluid is determined entirely by the conformational entropy of the material, the *Theory of Purely Entropic Elasticity* (*PEE*) emerged [1-3]. Under this premise, the internal energy density of any fluid particle, ε, was taken as a function of temperature only. In other words, the internal energy of a melt does not change when the melt is subjected to deformation, and the change in free energy due to orientation is entirely due to the change in entropy. The aim of this work is to test the validity of the *PEE* through a series of atomistic simulations of long chain alkane systems.

Approach

We investigated polydisperse systems of *n*-alkanes, with average chain lengths ranging from C_{24} up to C_{78}. The simulations were carried out using the End-Bridging Monte Carlo scheme (EBMC) of Pant and Theodorou [4], as implemented by Mavrantzas et al [5-7]. The melts were oriented using the uniaxial orienting field of Mavrantzas and Öttinger [7]. The chains were modeled using the united atom approach of Siepmann et al. [8]. The free energy of the melts was evaluated using two different approaches: via direct thermodynamic integration [7, 9] and from the FENE-P and the UCM visco-elastic models [10].

Results

Our results indicate that the free energy of the systems under investigation has contributions from both energetic and entropic origins. Moreover, we show that the relative magnitude of the energetic and entropic contributions has a strong dependence on temperature, orienting field strength and molecular weight. For example, the relative effect of the energetic to the entropic contributions tends to diminish with increasing molecular weight. All of these effects will be presented and discussed in detail, as well as their implications to the *Theory of Purely Entropic Elasticity*.

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