Rheology of liquid n-alkanes. Molecular dynamics calculation

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Modern industry is strongly interested in rheological properties of hydrocarbon liquids as main constituents of oils and fuels. The calculation of the transport coefficients for monoatomic systems has become a routine process [1], but in the case of complex liquids the application of classical methods faces difficulties [2, 3].

The self-diffusion coefficient of n-triacontane ($C_{30}H_{62}$) is calculated using Einstein-Smoluchowsky and Green-Kubo relations. We use three different force fields: TraPPE-UA (united-atom) [4], DREIDING (all-atom) [5] and OPLS-AA (all-atom, includes the Coulomb interaction) [6], for making sure that obtained results are not artefacts of a particular model. The molecule center of mass $\langle \Delta r^2(t) \rangle$ has a subdiffusive part ($\langle \Delta r^2(t) \rangle \sim t^\alpha$, $\alpha < 1$), caused by molecular crowding at low temperatures. Long-time asymptotes of molecule $\langle v(0)v(t) \rangle$ are collated with the hydrodynamic tail $t^{-3/2}$ demonstrated for atomic liquids [7]. The importance of these asymptotes are discussed. Parameters that provide the compliance of Einstein-Smoluchowsky and Green-Kubo methods are analysed. Temperature effects on the diffusion process are also treated. We compare results obtained using both equations with experimental data. The application of modified Stokes-Einstein equation for shear viscosity of polymers is presented. The molecular dynamics simulations are carried out in the LAMMPS package [8].

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