



Confined fluid density of a pentaerythritol tetraheptanoate lubricant investigated using molecular dynamics simulation



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ABSTRACT

Molecular and density distributions of the lubricant, pentaerythritol tetraheptanoate (PEC7), confined to a nanogap were investigated using molecular dynamics (MD) simulations at various temperatures, initial film thicknesses and pressures. All of the simulated film thicknesses were less than 10 nm. The PEC7 molecular orientation and density profiles were analyzed, and the simulated densities were compared with empirical bulk fluid densities. The results show that the PEC7 atoms tend to form two or three layers near every confining wall, but the PEC7 molecules orient randomly throughout the film. The lubricant density profiles are found to fluctuate frequently, and the distances between the layers of lubricant atoms are irregular. Furthermore, the equivalent density is lower for films with a thinner initial film at the same pressure and temperature, but the compressibility is similar for films with different initial film thicknesses. The simulated densities with an initial film thickness of 9.32 nm are in agreement with the values obtained from the Tammann–Tait equation, with deviations less than 5%. The MD simulation can not only predict the bulk compressibility of the lubricant but also provide information on the density and molecular distribution within a thin film, which cannot be obtained from experiments.

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1. Introduction

Fluid density and behavioral dependence of the fluid upon temperature and pressure are key criteria in lubricant selection. Density widely appears in the fundamental equations of hydrodynamic lubrication. The value of density is necessary to determine the experimental dynamic film thickness and viscosity of a lubricant [1,2]. For most engineering applications and designs, liquids are considered incompressible to facilitate solving the hydrodynamic equations, but in nanoscale hydromechanics and thin film lubrication mechanics, the density variation of a lubricant cannot be neglected, as it significantly influences the tribological behavior of the lubricant [1,3].

Both experimental and theoretical studies have indicated that the properties of thin film lubrication (TFL) cannot be determined by classical theories [1–4]. As film thickness approaches nano and molecular scales, the well-established continuum theories and the

hypothesis of uniform density distribution in the direction of film thickness fail to be valid. These deviations become more significant as the thickness of the lubricating film decreases.

Most of the published studies on thin film properties focused on boundary slip, viscosity and friction [5–9]. Studies relating to compressibility are limited. Although the thickness and dynamic force of a film can be obtained experimentally as the film approaches nano scale, it remains very difficult to measure density in a nanoscale fluid. The empirical models of density, such as the Aalto–Keskinen model [10], the Dowson–Higginson model [11], the Hankinson–Brobst–Thomson model [12], and the Tammann–Tait model [1,13], were developed by curve fitting macroscopic experimental data. Cibulka and Hnědkovský [14], Pecar and Dolecek [15], and Fandiño et al. [16–18] measured and developed correlations for densities of different fluids.

It is difficult to conduct density experiments at pressures greater than 700 MPa [1]. However, thin-film pressures in engineering elastohydrodynamic lubrication always exceed 3 GPa. With increasing computational power and the development of parallel molecular dynamics algorithms, studies based on molecular dynamics (MD) simulations have recently been introduced to investigate compressibility. However, most of these molecular dynamics simulations focused on the compressibility of solid-phase materials

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T	absolute temperature (K)
p	pressure (MPa)
h_0	initial film thickness (nm)
h	film thickness (nm)
q	atomic charge (e) – Eq. (1)
r	inter-particle distance (Å) – Eq. (1)
E	potential energy (kcal mol ⁻¹) – Eq. (1)
K	scale factor – Eq. (2)
A, B, C	Tammann–Tait coefficient – Eq. (6)

Greek letters

ρ	density (kg/m ³)
ε	energy parameter (kcal) – Eq. (1)
σ	distance parameter (Å) – Eq. (1)
θ	bond angle (rad) – Eq. (3)
ϕ	torsion angle (rad) – Eq. (4)
χ	out-of-plane angle (rad) – Eq. (5)

Subscripts

i, j, ij	atomic index
nonbond	nonbonding interaction
bond, angle, dihed, impro	intramolecular interaction

[19–22]. Examples of the few MD studies on liquid compressibility use simple hard-sphere fluid models [23], dissipative particle dynamics investigations [24], coarse-grained bead-spring models, and normal alkane models [2,25–28].

Not only have MD simulations observed that the atom and density distribution in nanoscale thin films are inhomogeneous, tending to form layers parallel to the confining walls, but experimental studies have as well. This phenomenon occurs in thin films regardless of whether the structure of the lubricant molecule is a spherical LJ particle, a short linear chain, a long linear chain, a branched chain or a ring chain [3,26,29–31]. Existing studies always consider the broadening of density profile peaks as their distance from the walls increased [3,29,32].

Pentaerythritol tetraheptanoate (PEC7) is an environmentally compatible lubricant because it is highly biodegradable, less toxic than mineral oils and manufactured from renewable resources. It is mainly used as a base oil in jet engines and air compressors due to its superior thermal stability, excellent antioxidant properties and low volatility.

In this study, MD simulations using the polymer consistent force field (PCFF) have been utilized to predict the compressibility of PEC7 for films with initial film thicknesses of 3.61, 6.37 and 9.32 nm at temperatures of 293 and 373 K and pressures in the range of $100 \leq p/\text{MPa} \leq 2400$. The simulated densities were compared with the traditional Tammann–Tait model densities [16] to investigate the feasibility of the MD model and the unique compressibility of thin film lubrication.

2. Model setup and simulation procedure

Two smooth face-centered-cubic lattice platinum (001) surfaces, containing 4096 Pt atoms, were used to confine a lubricant layer of PEC7. The lateral (xy) dimensions of every surface were kept constant at $6.28 \text{ nm} \times 6.28 \text{ nm}$ for all cases. The system was accommodated in a simulation box with periodic boundary conditions in the x - and y -directions. The details of the simulation box are shown in Fig. 1. A compressive load was applied to the upper wall with the lower wall fixed. The PEC7 ($\text{C}_{33}\text{H}_{60}\text{O}_8$) consists of four ester groups and four linear chains. Its molecular structure and model are presented in Fig. 2.

The initial system configuration was constructed using Materials Studio software. The initial film thickness, h_0 , was based on the PEC7 amorphous cell with an empirical bulk density $\rho = 995.9 \text{ kg/m}^3$ at temperature $T = 278.15 \text{ K}$ and pressure $p = 0.1 \text{ MPa}$ [16]. Three films with different initial thicknesses were considered, each with the same number of platinum atoms and different numbers of PEC7 lubricant molecules, namely, 58, 154 and 275, corresponding to initial film thicknesses of 3.61, 6.37 and 9.32 nm. As an example, the model system with $h_0 = 9.32 \text{ nm}$ consisted of a total of 31,871 atoms.

All MD simulations of the PEC7 compressibility were performed with the large-scale atomic/molecular massively parallel simulator (LAMMPS) [33,34]. The PCFF [35] was applied to determine the atomic interaction force, as it was accurate and applicable to the general class of organic, biomolecular, polymeric, and bioinorganic systems. The PCFF is a second-generation force field which is derived by fitting the experimental data and using quantum mechanical calculations. The total potential energy of PCFF can be divided into nonbonding interaction terms and valence terms. The nonbonding interactions between lubricant atoms and wall atoms and between pairs of nonbonded lubricant atoms include the van der Waals (vdW) Lennard-Jones (9–6) pair interaction and the Coulombic electrostatic interaction. The nonbonding potential is given by [33–36].

$$E_{\text{nonbond}} = \sum_{i>j} \varepsilon_{ij} \left[2 \left(\frac{\sigma_{ij}}{r_{ij}} \right)^9 - 3 \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \sum_{i>j} \frac{q_i q_j}{r_{ij}} \quad (1)$$

where r_{ij} is the distance between pair of i th and j th atoms. ε_{ij} and σ_{ij} represent the Lennard-Jones energy and distance parameters, respectively. q_i and q_j are the charges on the two atoms. The valence terms include bond stretching, angle, dihedral, and improper terms of lubricant intramolecular interactions and are given by

$$E_{\text{bond}} = \sum_b [K_{b2}(b - b_0)^2 + K_{b3}(b - b_0)^3 + K_{b4}(b - b_0)^4] \quad (2)$$

$$E_{\text{angle}} = \sum_{\theta} [K_{\theta2}(\theta - \theta_0)^2 + K_{\theta3}(\theta - \theta_0)^3 + K_{\theta4}(\theta - \theta_0)^4] + \sum_b \sum_{b'} K_{bb'}(b - b_0) + \sum_b \sum_{\theta} K_{b\theta}(b - b_0)(\theta - \theta_0) \quad (3)$$

$$E_{\text{dihed}} = \sum_{\phi} [K_{\phi1}(1 - \cos \phi) + K_{\phi2}(1 - \cos 2\phi) + K_{\phi3}(1 - \cos 3\phi)] + \sum_{\phi} \sum_b (b - b_0) [K_{\phi b1} \cos \phi + K_{\phi b2} \cos 2\phi + K_{\phi b3} \cos 3\phi] + \sum_{\phi} \sum_{b'} (b' - b'_0) [K_{\phi b'1} \cos \phi + K_{\phi b'2} \cos 2\phi + K_{\phi b'3} \cos 3\phi] + \sum_{\phi} \sum_{\theta} (\theta - \theta_0) [K_{\phi\theta1} \cos \phi + K_{\phi\theta2} \cos 2\phi + K_{\phi\theta3} \cos 3\phi] + \sum_{\phi} \sum_{\theta} \sum_{\theta'} K_{\phi\theta\theta'} (\theta - \theta_0)(\theta' - \theta'_0) \cos \phi \quad (4)$$

$$E_{\text{impro}} = \sum_{\chi} K_{\chi} \chi^2 + \sum_{\theta} \sum_{\theta'} K_{\theta\theta'} (\theta - \theta_0)(\theta' - \theta'_0) \quad (5)$$

In the above equations, K is the scale factor for the corresponding term; the parameters b , θ , ϕ , and χ represent bond, bond angle, torsion angle, and out-of-plane angle, respectively. The PCFF

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