A non-empirical free volume viscosity model for alkane lubricants under severe pressures

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Viscosities $\eta$ and diffusion coefficients $D_s$ of linear and branched alkanes at high pressures $P<$0.7 GPa and temperatures $T$=500-600 K are calculated by equilibrium molecular dynamics (EMD). Combining Stokes-Einstein, free volume and random walk concepts results in an accurate viscosity model $\eta(D_s(P,T))$ for the considered $P$ and $T$. All model parameters (hydrodynamic radius, random walk step size and attempt frequency) are defined as microscopic ensemble averages and extracted from EMD simulations rendering $\eta(D_s(P,T))$ a parameter-free predictor for lubrication simulations.

Knowledge-based design and optimization of liquid lubricants require a quantitative modelling of their rheological properties under relevant tribological conditions [1]. For instance, lubricants in roller element bearing and gear applications are subject to pressures of the order of GPa [2]. Traditional empirical viscosity models (such as Barus or Roeans equation) fail to describe $\eta(P)$ over the relevant pressure range [3] indicating that improved viscosity models for the extreme pressure regime [4, 5] should be based on physical insights [6]. A promising approach employs the Stokes-Einstein relation [7]

$$D_s = k_B T/(n \pi \eta R_h) \quad (1)$$

that connects the viscosity with the self-diffusion coefficient $D_s$. Here, $R_h$ denotes the hydrodynamic radius and $n$ lies between the slip and no-slip hydrodynamics limits, 4 and 6. The applicability of Eq. (1) on a microscopic level has been theoretically motivated and is well established under normal conditions [8, 9], also for nonspherical molecules if $R_h$ is considered a free parameter. However, a breakdown of Stokes law has been observed in various dense liquids, including molecular glass formers [10, 11]. The mechanism of this breakdown is still subject to extensive research, mostly focused on densification obtained by supercooling [12–14]. This raises the question whether Eq. (1) remains valid for liquids which are densified by pressurisation instead of cooling.

In this letter, EMD simulations are utilized to validate Eq. (1) for linear and branched alkanes (constituents of ordinary lubricant base stock) for a pressure and temperature range representing typical tribological high load applications. We suggest a microscopic definition of

$$R_h = \sqrt{\langle a \rangle}/\pi \quad (2)$$

by introducing an EMD averaged molecular cross section $\langle a \rangle$. This represents an important step towards a parameter-free structure-property relationship (SPR) relating molecular structure with macroscopic viscosities.

Employing Eq. (1) necessitates an additional SPR for $D_s$. Here, we utilize the free volume (FV) concept [15, 16]

$$D_s = D_0 \exp(-v_c/v_f) \quad (3)$$

with the mean FV per molecule $v_f$ and the critical volume $v_c$. Note, that since $v_f$ is determined by the lubricant density $\rho$ an equation of state $\rho(P)$ is required to arrive at a pressure dependent viscosity law.

Although widely used for soft matter systems [17–19], the FV concept is being challenged due to concerns about the relevance of FV compared to energetic effects and about the physical interpretation of the free parameters $D_0$ and $v_c$ [20–24]. We show in the second part of this letter that Eq. (3) can be applied to our alkane lubricants and suggest microscopic definitions of $D_0$ and $v_c$. The latter relies on the observation that self-diffusion can be considered a random walk of a molecule’s center of mass (COM) with step length and attempt frequency determined by EMD simulations.

Two linear alkanes and three poly-$\alpha$-olefines (PAO) (for structures see Fig.1a) are modelled with the all-atom optimized potentials for liquid simulations (AA-OPLS) [25]. The EMD of these lubricants is simulated within a constant volume subject to periodic boundary conditions for densities ranging roughly from 470 to 850 kg/m$^3$. Time integration is performed employing the LAMMPS software suite [26, 27] with timestep 0.5 fs, and a Nosé-Hoover thermostat with relaxation time 0.1 ps [28, 29]. Viscosities $\eta$ are determined via the Green-Kubo formalism and self-diffusion coefficients $D_s$ via the mean squared displacement (MSD) [4] (see supp. Figs. S1/2).

As shown in Fig.1c, results for $\eta$ and $D_s$ vary over 3 orders of magnitude and are fully compatible with Eq. (1) (assuming slip boundary conditions $n=4$ [8, 9]). A parameter-free quantitative agreement is achieved by introducing the hydrodynamic radius via Eq. (2) as follows. Since the Stokes drag on macroscopic solid objects with slippery surfaces scales with the object’s cross section in the direction of a displacement [30], we calculate a directional molecular cross section $a$ as indicated in Fig.1d. To each molecule a volume $v_{mol}$ is assigned using a coarse grained hard sphere approach based on a CH$_X$ ($X = 1, 2, 3$) united atom representation [31] (see details in supp. Fig. S3). Then the molecule is displaced over a short distance $\varepsilon$ and its effective cross section area...
is defined by \( a = \Delta V/\epsilon \), where \( \Delta V \) is the newly occupied volume. Finally, the mean cross section is obtained by \( \langle a \rangle = \int q(a) da \), where \( q(a) \) is the probability for the molecule to have a configuration with cross section \( a \). Interestingly, \( \langle a \rangle \) scales linearly with the molecule size, despite the different morphologies (i.e. number of branches in alkanes - see inset in Fig. 1b). This scaling can be rationalized by a cylindrical shape estimate of long alkane chains, neglecting the contribution of chain ends and knots (supp. Fig. S4).

After having established a parameter-free relation between \( \eta \) and \( D_s \), we now focus on the diffusive motion of the alkanes. Fig. 2b shows part of a \( C_{10}\)-trimer COM trajectory with a behaviour which is characteristic of a caging effect. The COM position oscillates within a compact volume due to confinement by the neighboring molecules (snapshots 1,3,5 of Fig. 2a). Elementary diffusion steps (EDS) take place via occasional irreversible translations (indicated by red arrows in snapshots 2,4,6 of Fig. 2a). The FV ansatz leading to Eq. (3) assumes that the probability for an EDS is given by \( p(v_c) = \exp(-v_c/v_f) \). Here, \( v_c \) is the critical void size in the cage formed by a molecule’s neighbours allowing for an irreversible COM jump. Following the simple argument that this void has to accommodate the molecule, the critical volume \( v_c \) is expected to be of the order of the hard core molecule volume \( v_{mol} \). Note, that \( p(v_c) \) depends parametrically on the mean free volume per molecule \( v_f = \bar{v} - v_{mol} \), where \( \bar{v} \) denotes the molar volume [16].

Indeed, the self diffusion coefficient follows the form Eq. (3), as shown in Fig 2b, where lines are best fits for the 600K data. Fig. 2c displays the dependence of the fit parameters \( \bar{v} \) and \( D_0 \) on the size of the molecules. Surprisingly, the critical volume is about 3 times larger than \( v_{mol} \) in contradiction to the simple argument stated above. An alternative interpretation of \( \bar{v} \) is based on the following consideration. To perform an EDS, a molecule needs to move from its cage center to a void in the cage wall. The necessary critical volume for this displacement over the cage size \( r_c \) is then \( r_c \cdot \bar{v} \) with \( \bar{v} \) the molecule’s cross section. For constant \( a \) and \( r_c \), the diffusion process could then be pictured as a random walk with stepsize \( r_c \) and step frequency \( 1/\Delta t \). The latter is the product of an attempt frequency \( 1/\tau_0 \) and the success probability \( \exp(-r_c/a_rv_f) \) resulting in

\[
D_s(a,r_c) = r_c^2/(6\Delta t) = r_c^2/(6\tau_0) \exp(-r_c/a_rv_f). \tag{4}
\]

However, both \( a \) and \( r_c \) depend a priori on the molecules’ configurations with respect to the direction of the EDS. Fluctuating shapes and distances in molecular fluids result in a probability distribution \( q(a,r_c) \) for \( a \) and \( r_c \) that determine the diffusion coefficient \( D_s(a,r_c) \) in a certain direction and thus the total diffusion coefficient is \( D_s = \int D_s(a,r_c) q(a,r_c) da dr_c \). In the following, we demonstrate by sampling \( q(a,r_c) \) over all possible configurations and orientations that the first moments \( \langle a \rangle = \int aq(a,r_c) da dr_c \) and \( \langle r_c \rangle = \int r_cq(a,r_c) da dr_c \) dominate the diffusion process:

\[
D_s \approx \langle r_c \rangle^2/(6\tau_0) \exp(-\langle r_c \rangle/a_rv_f). \tag{5}
\]

For a given configuration, Eq. (4) implies a direction dependent stepsize and success probability for an individual...
FIG. 2. Dependence of diffusion on free volume. (a) Part of a C₁₀-trimer trajectory within bulk fluid at 0.6 MPa. Light blue: C-atoms; large dark blue: COM position; small violet: all COM positions (every 1 ps during 85 ps). The COM diffusive motion (arrows) can be described by a random walk between caged positions due to the confining presence of the surrounding molecules (not displayed). (b) Self diffusivity coefficient $D_s$ vs. inverse of the mean free volume per molecule $v_f = v - v_{mol}$ (colors as in Fig. 1). (c) $D_s$ values are best fits of $D_s = D_0 \exp(-v_c/v_f)$ on 600 K data. (f) Fit results $D_0$ and $v_c$; errorbars: 68% confidence interval.

EDS. To study this anisotropy we consider an auxiliary system of preferentially oriented alkane immersed in a bath of unconstrained molecules. This artificial test situation is realized for $n$-hexadecane at two different densities by applying opposing external forces $±0.05\,eV/\AA$ to the head and tail carbon atoms of 2.6% of the molecules (Fig. 3a). The resulting preferential orientation leads to a permanently anisotropic cross section $a(\theta)$ (Fig. 3b) and cage radius $r_c(\theta)$ (red dots in Fig. 3b), where $\theta$ denotes the angle between the applied forces and the EDS direction. Here, $a(\theta)$ was calculated as previously defined (see Fig. 1b) for a given direction $\theta$. Lacking an unambiguous definition of $r_c(\theta)$, a pragmatic estimate was based on the direction dependent radial distribution function $g_{CD}(\theta,r)$ of the molecules’ COM (Fig. 3c) via $g_{COM}(\theta,⟨r_c(\theta)⟩) = 1$. In the same spirit, the isotropic cage size $⟨r_c⟩$ (circle in Fig. 3c) was determined from the isotropic radial distribution function $g_{COM}(r)$ (bold line in Fig. 3c). Note, that this value is close to the result obtained via $r_c = \int ⟨r_c(\theta)⟩ d\cos \theta$.

As expected the preferentially oriented molecules exhibit a pronounced anisotropy in the MSD $⟨r^2(\theta)⟩$ (Fig. 3d) and consequently in the diffusion coefficient $D_s(\theta)$. Interestingly, the mean diffusion coefficient $D_s = (D_s(\theta = 0) + 2D_s(\theta = \pi/2))/3$ is equal to the isotropic diffusion coefficient of the unperturbed molecules, confirming that diffusion is given by an average over all directions with respect to the main axis of a hexadecane molecule. Most importantly however, $D_s(\theta)$ scales with the respective static structure properties as predicted by Eq. 5 validating the applicability of a FV ansatz on the microscopic level of an EDS (Fig. 3e).

Comparing Eq. 5 with 6 leads to $D_0 = ⟨r_c⟩^2/(6τ_0)$ and $v_c = ⟨r_c⟩/⟨a⟩$. Indeed, applying the above structure evaluation for $a(\theta)$ (inset in Fig. 1b) and $r_c$ (Fig. 3b) to the unperturbed systems of all 5 fluid types reveals that the product $v_c = ⟨r_c⟩/⟨a⟩$ agrees well with the fitted critical volumes $\tilde{v}_c$ (Fig. 3a inset). Both, $a(\theta)$ and $⟨r_c⟩$ are only weakly dependent on density and temperature (supp. Figs. 5/6) and can be conveniently estimated from an EMD simulation for a single $\rho$ and $T$.

The remaining free parameter $τ_0$ (time between random walk attempts) can be interpreted as the time scale for structure decorrelation in the molecule/cage system. The connection between structural relaxation, diffusion and viscosity is subject of ongoing research 33, and fully unravelling the underlying mechanisms goes far beyond the scope of this work. Nevertheless, as a starting point we consider the time autocorrelation function $⟨\mathbf{e}(0) \cdot \mathbf{e}(t)⟩$ of the molecules’ end-to-end vector orientation $\mathbf{e}(t)$ (see Fig. 3b) to quantify the intramolecular structure decorrelation. For long hydrocarbon chains, $⟨\mathbf{e}(0) \cdot \mathbf{e}(t)⟩$ is well described by a double exponential function 34

$$<e(0) \cdot e(t)> = Ce^{-t/\tau_a} + (1 - C)e^{-t/\tau_b}$$

with two separate characteristic decay times $\tau_a$ and $\tau_b$. 

FIG. 3. Diffusion of artificially oriented n-hexadecane molecules in an unconstrained bath. (a) Superimposed configurations of one randomly chosen bath and one oriented molecule ($±F_{app}$ applied along $\theta = 0, \pi$, COM motion subtracted, 1 frame/ns). (b) Mean cross section $a(\theta)$ for unconstrained (“•”) and constrained (“○”) molecules, unperturbed value $a(0)$ (see Fig. 1). (c) $θ$-dependent COM radial distribution function (shifted for better visibility) with estimate of cage radius $r_c(\theta)$ (“○”); same for isotropic COM-RDF of bath molecules (bold line, “•”). (d) Anisotropic MSD for oriented molecules in least dense system. (e) Anisotropic self-diffusion coefficient $D_s(θ)$ (2 different densities “•, ○”) normalized with static structure properties according to Eq. 5. Direction averaged values $D_s = (D_s(0) + 2D_s(\pi/2))/3$, isotropic $D_s$ of bath molecules and of unperturbed systems (“+,” “□”) are identical.
On the one hand, a long time decay is observed on the time scale of the diffusion process $\tau_\alpha \approx \Delta t = r_c^2/(6D_0)$, ranging from 10 ps - 1 ns. On the other hand, $\tau_\beta$ is of the order of 1 - 10 ps and is insensitive to the fluid density (within statistical uncertainties, see supp. Fig. S7). This $\beta$-relaxation time fits well with the expected attempt frequency for the random walk $\tau_\alpha \approx \tau_0 = r_c^2/(6D_0)$ as illustrated in Fig. 4d, which suggests it as a good measure for the relevant structure decorrelation on short times.

The presented results are further validated in a series of scaling tests with modified model parameters for both intra- and intermolecular interactions (supp. Fig. S8). In particular, the strength of nonbonded interactions has little influence, but a scaling of the atomic radii $\sigma_{LJ}$ results in strong variations of the diffusivity caused by the exponential term in Eq. [6]. Moreover, the prefactor $D_0$ is sensitive to variations of the energy barrier for bond rotation, which influences intramolecular relaxations. All scaling tests are also in quantitative agreement with the Stokes-Einstein relation, supporting our definition of a hydrodynamic radius in Eq. [4].

Finally, combining Eqs. [1], [2] and [3] the viscosity can be expressed as a function of density

$$\log \frac{\eta(T, \rho)}{\eta_0(T)} = \frac{\langle r_c \rangle/\langle a \rangle}{v_{mol}} \left( \rho_m/\rho - 1 \right)$$

with $\rho_m = M/v_{mol}$ the maximum hypothetical density for zero free volume ($1 - v_f/v = \rho/\rho_m$; supp. Fig. S4). Apart from the density, the r.h.s. contains only equilibrium structure properties, namely the molecules' volume $v_{mol}$, mean cross section $\langle a \rangle$ and mean next neighbor distance $\langle r_c \rangle$. The temperature dependence of $\eta$ enters via $\eta(T) = 1.5k_BT\tau_0(T)/\langle r_c^2/\sqrt{\pi\langle a \rangle} \rangle$. By employing Eq. [7] and identifying $\tau_0$ with $\tau_\beta$ a parameter free rescaling of the simulated viscosities can be established (Fig. 4b). This scaling law can also be applied to experimental high $T$ and $P$ viscosity data for $n$-dodecane [32]. We find a good agreement of the experimental data with our parameter-free viscosity model Eq. [7] (inset of Fig. 4b).

To conclude, a combination of basic random walk and FV theory fully describes the self diffusion mechanism of long alkane chains, linear and branched alike, in the high $T$ and $P$ regime. A crucial part of the presented work is the introduction of the mean cross section $\langle a \rangle$ and mean cage size $\langle r_c \rangle$ as novel molecule shape parameters. While $\langle a \rangle$ establishes a quantitative link between viscosity and self diffusion via the Stokes-Einstein relation, $\langle a \rangle$ and $\langle r_c \rangle$ allow for a parameter-free density scaling of both transport coefficients. The viscosity model can be directly implemented in density-based Reynolds-solvers [35] and will contribute to a new cutting-edge simulation tool for tribological applications. The proposed shape parameters also opens new possibilities to quantify the role of molecular structure on rheology in anisotropic situations, such as shear thinning [36, 37] or in nanometer-thin boundary lubrication films [38]. Our approach might also be useful for other soft materials, such as self assembled membranes [17, 18], polymer-solvent systems [19] or adsorbates in nanopores [39].

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