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Rotational viscosity of a liquid crystal mixture: a fully atomistic molecular dynamics study*

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Fully atomistic molecular dynamics (MD) simulations at 293, 303 and 313 K have been performed for the four-component liquid crystal mixture, E7, using the software package Material Studio. Order parameters and orientational time correlation functions (TCFs) were calculated from MD trajectories. The rotational viscosity coefficients (RVCs) of the mixture were calculated using the Nemtsov–Zakharov and Fialkowski methods based on statistical-mechanical approaches. Temperature dependences of RVC and density were discussed in detail. Reasonable agreement between the simulated and experimental values was found.

Keywords: rotational viscosity, molecular dynamic simulation, nematic liquid crystal, mixture
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1. Introduction

The integration of anisotropy and fluidity makes liquid crystals (LC) truly fascinating materials, and extremely suitable for modern electro-optic applications.[1−5] Over the past few decades, liquid crystal displays (LCDs) have become the dominant flat panel display technology.[6,7] The liquid crystalline material also plays an important role in a variety of other optical devices, e.g. phase modulators for real time wave front control in adaptive optics systems,[8,9] and optical waveguides, routers and interconnects for optical communication.[2,10] In order to obtain an optimal performance, a certain set of physicochemical requirements has to be met by the LC materials, such as broad nematic phase range, low rotational viscosity, appropriate dielectric anisotropy and birefringence, etc. In fact, almost no single compound could fulfill all of these requirements, so practical liquid crystal materials are usually a mixture, which typically contains 10–20 compounds.[6,11] The development of new LC compounds is not an easy task, due to the limited knowledge about the structure–property relationships. In practice, some simple empirical rules together with trial and error approaches usually can be relied on to help the design of molecular structure and the mixing process. Recently, a lot of theoretical studies, based on computer simulation, have been performed in order to shed light on the connections between macroscopic properties and the molecular structure.[12−14] A notable advantage of the simulation method is that it can be used to investigate properties which are difficult to explore experimentally and to predict certain properties for optimization so as to remove the need for costly and time-consuming synthesis of a mass of compounds.

It has been reported that the estimation of dielectric and optical anisotropy of LC compounds are reasonable by using the semiempirical molecular orbit method (AM1), on the basis of the well-known Vuks and Maier–Meier theory.[15,16] Another useful property for the application of nematic liquid crystals is the rotational viscosity coefficient (RVC), γ_1, which dominates the switching time of most liquid crystal devices. The γ_1 is difficult to obtain from simulations due to the long simulation lengths needed to produce good statistics. Many previous studies are based on the Gay–Berne model, in which the molecule is represented by a Lennard–Jones 12-6 potential.[17−20] Although allowing large numbers of molecules to be simulated at a time, it seems that this over-simplified model cannot reproduce in full the realistic properties.

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By contrast, the atomistic model, in principle, affords us the possibility to reproduce the actual properties of a molecular system.[21] In this paper, we will conduct molecular dynamics (MD) simulation of a typical liquid crystal mixture at the fully atomistic level and focus our attention on the rotational viscosity property.

The calculation of RVC can be carried out by either equilibrium or non-equilibrium MD simulation. Sarman and co-workers[22−25] used both equilibrium Green–Kubo type formulas and non-equilibrium MD approach. Another non-equilibrium MD technique was proposed by Kuwajima,[26] in which the director of nematic systems is forced to rotate by an artificial force, termed as aligning force. Zakharov *et al*[27−29] computed the RVCs of 5CB and 8OCB by equilibrium MD modeling, under the framework of statistic mechanical methods based on the rotational diffusion coefficient (RDC). Cheung *et al*[30] conducted equilibrium MD modelling on PCH5 using a fully atomistic model. The rotational viscosity calculated from the director angular velocity correlation function and the director mean-squared displacement confirms the experimental values. Caper *et al*[31,32] method is similar to that of Zakharov. The temperature-and size-dependency, and the odd-even effect of RVC of the *n*CB series were studied. All of these studies concentrated on simple mono-component LC. While, the question is that almost all practical LC materials are a mixture as mentioned above. In the present work, we will conduct a fully atomistic MD simulation for the LC mixture E7 at different temperatures and calculate its rotational viscosity for the first time, as far as we know. E7 supplies us a straightforward test system, because it consists of only four components and their molecular constitutions are extremely similar to each other. Both the mixture itself and its components have been extensively studied and well-parameterized in the literature.

This paper is organized as follows: The details of the MD simulation are described in Section 2. The calculating methods of RVC are briefly summarized in Section 3. Then the results and discussion are collected in Section 4. We draw some conclusions in the last section.

2. MD simulation details

E7 has four components: 4-cyano-4'-*n*-pentyl-biphenyl (5CB), 4-cyano-4'-*n*-heptyl-biphenyl (7CB), 4-cyano-4'-*n*-octyloxy-biphenyl (8OCB) and 4-cyano-4"-*n*-pentyl-*p*-terphenyl (5CT). The molecular numbers of each component were set according to the approximate weight percentage composition of the mixture (see Table 1). In total, 256 molecules were contained in a cubic lattice and a nematic phase was constructed assisted by the amorphous cell tool, which is a module of the software package Material Studio.[33] Then, MD equilibrations were performed using the discover tools. The initial density was set to 1 $\mathrm{g\cdot cm^{-3}}$. Periodic boundary condition was utilized to eliminate the border effect.

Table 1. Composition of the E7 mixture in terms of the percentage in weight of each component and the number of molecules corresponding to each type in the MD simulation.

type of molecule	weight percentage	No. of molecule
5CB	51	141
7CB	25	62
8OCB	16	36
5CT	8	17

The polymer consistent force-field (PCFF) force field[34] was employed in our MD simulations, with each atom in the molecule treated explicitly. The potentials of the force field take the form

$$
\begin{aligned}
E_{\mathrm{ff}} = & \sum_{b}\left[K_2\left(b-b_0\right)^2+K_3\left(b-b_0\right)^3+K_4\left(b-b_0\right)^4\right]+\sum_{\theta}\left[H_2\left(\theta-\theta_0\right)^2+H_3\left(\theta-\theta_0\right)^3+H_4\left(\theta-\theta_0\right)^4\right] \\
& +\sum_{\phi}\left\{V_1\left[1-\cos\left(\phi-\phi_{10}\right)\right]+V_2\left[1-\cos\left(\phi-\phi_{20}\right)\right]+V_3\left[1-\cos\left(\phi-\phi_{30}\right)\right]\right\} \\
& +\sum_{\chi}K_\chi\chi^2+\sum_{b}\sum_{b'}F_{bb'}\left(b-b_0\right)\left(b'-b'_0\right)+\sum_{\theta}\sum_{\theta'}F_{\theta\theta'}\left(\theta-\theta_0\right)\left(\theta'-\theta'_0\right) \\
& +\sum_{b}\sum_{\theta}F_{b\theta}\left(b-b_0\right)\left(\theta-\theta_0\right)+\sum_{b}\sum_{\phi}\left(b-b_0\right)\left[V_1\cos\phi+V_2\cos 2\phi+V_3\cos 3\phi\right]
\end{aligned}
$$

$$+\sum_{b'}\sum_{\phi}(b'-b'_0)\left[V_1\cos\phi+V_2\cos 2\phi+V_3\cos 3\phi\right]+\sum_{\theta}\sum_{\phi}(\theta-\theta_0)\left[V_1\cos\phi+V_2\cos 2\phi+V_3\cos 3\phi\right]$$
$$+\sum_{\phi}\sum_{\theta}\sum_{\theta'}K_{\phi\theta\theta'}\cos\phi\,(\theta-\theta_0)\,(\theta'-\theta'_0)+\sum_{i>j}\left[\frac{A_{ij}}{r_{ij}^9}-\frac{B_{ij}}{r_{ij}^6}\right]+\sum_{i>j}\frac{q_iq_j}{\varepsilon r_{ij}}, \quad (1)$$

where b, θ and ϕ represent bond length, bond angle and dihedral angle respectively, and the subscript 0 denotes the value in the equilibrium state. K, H and V are respectively force constants of bond stretching, bond angle bending and torsional rotations. Both bond and angle terms contain anharmonic constants in quartic terms to characterize anharmonic features. The torsion function is represented by a symmetric Fourier expansion. The 4-th term represents out-of-plane bending and the 5-th–11-th terms refer to the coupling between two internal coordinates. Nonbonded interactions are represented by the last two terms. A Lennard–Jones 9-6 potential represents the Van der Waals energy, while the electrostatic interaction has a form of classic Coulomb formula. A_{ij} and B_{ij} are Lennard–Jones coefficients; q_i and q_j are partial charges, for atoms i and j respectively.

Initially, the system was minimised by conjugate-gradients algorithm, until the maximum energy deviation was less than 1 kcal $\cdot$ mol^{-1}. MD simulation was then performed in isothermal–isobaric (NPT) ensemble, by using the Berendsen thermostat and barostat. Pressure was confined to 1.01×10^5 Pa during the MD simulation. The behaviour of molecules under different temperatures, at 293, 303 and 313 K, was investigated. The long-range electrostatic interactions were evaluated by Ewald summation, with the accuracy of convergence being 0.001 kcal $\cdot$ mol^{-1} and the update width 3 Å (1 Å = 0.1 nm). While the short-range Van der Waals interactions were truncated using an atom-based cutoff of 9.5 Å. In total 3 ns MD equilibration was carried out at each temperature with a time-step of 1 fs. The data of the last 500 ps were collected for trajectory analysis.

3. Computational method of RVC

A number of methods can be used to calculate the RVC of nematic liquid crystals.[22,26,27,35,36] In this study we adopt the two statistical–mechanical approaches proposed by Nemtsov–Zakharov[27] and Fialkowski[36] respectively. Although based on different physical models, the expressions of RVC in these methods have a similar form. Both of them are proportional to the temperature T, molecular number density $\rho = N/V$, and inversely proportional to the rotational self-diffusion coefficient $D_\perp$.

The approach of Nemtsov and Zakharov (NZ)[27] is based on the random walk theory together with some ideas of the Zubarev nonequilibrium statistical operator. It is a correction to its predecessor by considering the additional correlation of the stress tensors with the director and fluxes with the order parameter tensor, except the autocorrelation of the microscopic stress tensor. The RVC is expressed in the form

$$\gamma_1^{\mathrm{NZ}}=\frac{\rho kT}{D_\perp}g_{\mathrm{NZ}}(\bar{P}_2), \quad (2)$$

where k is Boltzmann constant, $\bar{P}_2$ is the second-rank order parameter and $g_{\mathrm{NZ}}(\bar{P}_2)$ is a rational function

$$g_{\mathrm{NZ}}(\bar{P}_2)=3\bar{P}_2^2\frac{3.181+0.757\bar{P}_2}{2.181+\bar{P}_2+12.56\bar{P}_2^2+4.69\bar{P}_2^3-0.743\bar{P}_2^4}. \quad (3)$$

Fialkowski (F)[36] proposed a rotational diffusion model which was originally for biaxial molecules. It was also based on changes in the Helmholtz free energy caused by the shear flow. In the limit case, the biaxial property vanishes and the system becomes uniaxial. The expression for the RVC of uniaxial nematics can be written as

$$\gamma_1^{\mathrm{F}}=\frac{\rho kT}{D_\perp}g_{\mathrm{F}}(\bar{P}_2,\bar{P}_4), \quad (4)$$

where

$$g_{\mathrm{F}}(\bar{P}_2,\bar{P}_4)=\frac{35\bar{P}_2^2}{16\bar{P}_4+5\bar{P}_2+14}, \quad (5)$$

$\bar{P}_4$ is the fourth rank order parameter.

A convenient method to compute the rotational self-diffusion coefficient $D_\perp$ is as follows:[27]

$$D_\perp=\left(6\tau_{00}\frac{7+5\bar{P}_2-12\bar{P}_4}{7+10\bar{P}_2+18\bar{P}_4-35\bar{P}_2^2}\right)^{-1}. \quad (6)$$

The correlation time τ_{00} can be derived by fitting the normalised orientational time correlation function

(TCF) from the trajectory analysis of an MD simulation.

TCF is an appropriate function to characterize the rotational dynamics of nematogen:

$$\Phi^L_{mn}(t) = \frac{\left\langle D^{L*}_{mn}(\Omega(0))\, D^L_{mn}(\Omega(t))\right\rangle}{\left\langle D^{L*}_{mn}(\Omega(0))\, D^L_{mn}(\Omega(0))\right\rangle}, \qquad (7)$$

where $D^L_{mn}(\Omega)$ is the Wigner rotational matrix of rank L and $\Omega = (\phi, \theta, \psi)$ is a set of Euler angles that define the orientation of the molecular axis relative to the director frame. For symmetrical liquid crystalline molecules in its nematic phase, it just corresponds to the tumbling motion when $m = n = 0$ for the second rank ($L = 2$) TCF and usually can be fitted by a single exponential approach,

$$\Phi^2_{00} = \Phi^2_{00}(\infty) + \left[\Phi^2_{00}(0) - \Phi^2_{00}(\infty)\right] \exp\left(-\frac{t}{\tau_{00}}\right). \qquad (8)$$

The second and fourth rank order parameters are ensemble and time-averaged values, given by

$$\bar{P}_2 = \frac{3\overline{\cos^2\theta} - 1}{2},$$
$$\bar{P}_4 = \frac{35\overline{\cos^4\theta} - 30\overline{\cos^2\theta} + 3}{8}, \qquad (9)$$

where $\cos\theta = \boldsymbol{u}\cdot\boldsymbol{n}$. The vector $\boldsymbol{u}$ indicates the direction of molecular long axis which corresponds to the smallest eigenvalue of the rotational inertia tensor. The director $\boldsymbol{n}$ is the eigenvector associated with the largest eigenvalue of the second-rank ordering tensor:

$$Q_{\alpha\beta} = \frac{1}{2N}\sum_{i=1}^{N}(3u_{i\alpha}u_{i\beta} - \delta_{\alpha\beta}) \quad \alpha,\beta = x,y,z. \qquad (10)$$

4. Results and discussion

The four-component liquid crystal mixture E7 has a broad mesophase, which exists at about –30 °C to 58 °C.[37] In order to keep the model system in its nematic phase, our MD simulations were conducted at 293, 303 and 313 K respectively. Figure 1 shows a snapshot of the arrangement of 256 molecules at the final stage of 3 ns MD equilibration at 293 K, in which an obvious orientational order can be found.

We define the molecular long axis as the eigenvector corresponding to the smallest eigenvalue of the inertial tensor. These axes are used to calculate the orientational time correlation function from the trajectory of MD simulation. Figure 2 shows the TCFs of the mixture at 293, 303 and 313 K respectively. Since the first decay of TCF is not a one-exponential function and it does not correspond to the small step diffusion,[27] we fit the TCF by a single exponential function (see Eq.(8)) in the time interval 50–500 ps. The fitting results of TCFs, together with the order parameters, density and RDCs, are presented in Table 2.

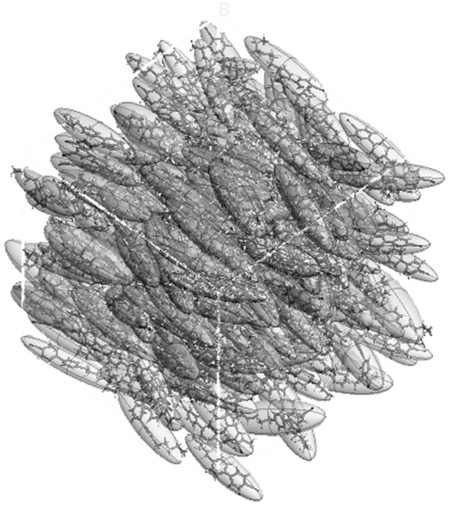


Fig.1. Snapshot of molecule arrangement of E7 after 3 ns MD equilibration at 293 K. (In total 256 molecules are contained in the box.)

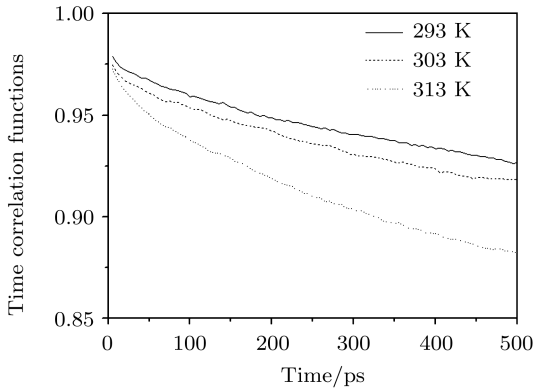


Fig.2. Normalised orientational time correlation functions of E7 at 293 K, 303 K and 313 K, respectively.

The rotational viscosity coefficients calculated by NZ and F methods are close to each other, although they depend on different physical models. In comparison with the measured rotational viscosity in Ref.[38], the calculated results at 293 K are in the same order, but a little underestimated. This is not surprising because a lot of approximations were adopted in the NZ or F theory. Similar results can also be found in other studies for 5CB or PCH5.[27,28,30,31] Furthermore, the MD simulation is not a very successful method to investigate the macroscopic properties of liquid crystal,

Table 2. Rotational viscosity coefficients for E7 calculated using Nemtsov–Zakharov (NZ) and Fialkowski (F) methods at 293, 303 and 313 K respectively.

T/K	$\bar{P}_2$	$\bar{P}_4$	ρ ($g \cdot cm^{-3}$)	τ_{00} (ps)	$D_\perp$ ($\times 10^8$ s^{-1})	γ_1^{NZ} (mPa·s)	γ_1^{F} (mPa·s)	$\gamma_1^{Exp\ a}$ (mPa·s)
293	0.76	0.37	0.9560±0.0060	434.9	0.629	70.36	117.06	282.8 (20.3 °C)
303	0.73	0.34	0.9514±0.0046	370.1	1.212	36.74	59.25	123.9 (33.3 °C)
313	0.70	0.32	0.9463±0.0045	304.5	2.145	20.81	32.29	53.9 (46.9 °C)

[a] Ref.[38]

like order parameters. As shown in Table 2, the second rank order parameter at 293 K are 0.77, while the refractive index measurement yields a value 0.65 for E7.[39] From Eqs.(2)–(6), we can see that γ_1^{NZ} and γ_1^{F}, as well as $D_\perp$, all have a close relationship with the order parameters.

In Fig.3, the γ_1 of E7 is shown as a function of temperature. The experimental rotational viscosity decreases with temperature. We obtain similar variations from both NZ and F methods. The variations of order parameters and RDC, as well as density of the mixture agree well with those from experiments too, they decrease as temperature rises (see Table 2). The temperature dependence of these quantities has been investigated extensively by MD simulation before, but consistency of variation with experiment was rarely observed.[30,31] In MD simulation, force field parameters, sample size and simulation time are effective methods to obtain a better result for liquid crystals. It is noticeable that the total molecule number is 256 and the MD equilibration time is 3 ns in our simulation, both of which are almost 2 times larger than that of previous studies at an atomistic level. The predictions about the system size effects on macroscopic properties are controversial. In some articles size dependence of certain macroscopic quantity was found, while in others it was not.[40,41] Capar *et al*[31] reported that the order parameters and RDC vary remarkably while the rotational viscosities vary very slightly on doubling the number of molecules. Recently, some extremely long MD simulations have been conducted. Pelaez and Wilson[39] found that it takes about 100 ns for the mixture E7 to reach a stable nematic phase. This indicates that the MD equilibration time of several nanoseconds is not adequate, even thought the result here looks reasonable. A better prediction can be expected if the MD runs on the timescale of 100 ns. The density from our MD simulation is under-estimated too, as compared with the experimental value in the literature, which is 1.03 $g \cdot cm^{-3}$,[42] suggesting that the attraction between molecules may be very slightly too low in our model. In other studies,[30,39] the density was found overestimated sometimes. This is probably due to that, nowadays, most of the available force fields used in MD simulations are not derived from liquid crystals. It has been proved that more elaborated force field for a subset of common liquid crystals can give a better prediction of the macroscopic properties.[43]

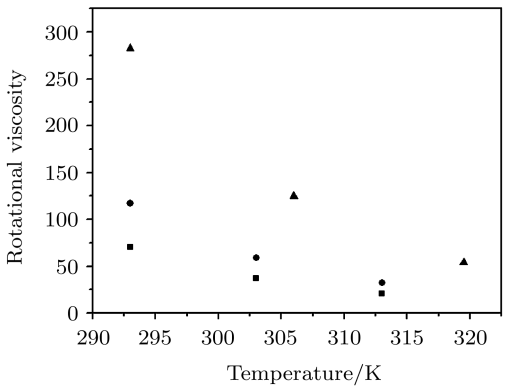


Fig.3. Temperature dependence of the rotational viscosity for E7. ■,γ_1^{NZ}; •,γ_1^{F}; ▲, γ_1^{Exp}(taken from Ref.[38]).

5. Conclusion

In this paper, the rotational viscosity coefficient of E7 in the nematic phase has been calculated by combination of fully atomistic molecular dynamic simulation technique and existing statistical-mechanical methods. This is the first time that the rotational viscosity coefficient of a liquid crystal mixture has been calculated by atomistic level MD simulation as far as we know.

The calculated NZ and F rotational viscosities are in the same order of magnitude as the experimental values and close to each other. The temperature dependences of RVC, as well as density, have also been

studied at 293, 303 and 313 K respectively. They vary consistently with experimental observation, although slightly under-estimated. Larger number of molecules, longer simulation time and revised force field for liquid crystals are expected to be helpful for improving this prediction.

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