

*Invited Paper*

# Magnetic field induced reduction of intermolecular force between the normal alkanes

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**Abstract:** Magnetic field can significantly change the characteristics of alkanes and related petroleum products, and the physical mechanism has received much attention for several years. Terahertz time-domain spectroscopy (THz-TDS) is employed in this paper to characterize the optical parameters and diamagnetic anisotropy properties of liquid normal alkanes (n-alkanes) under the action of a magnetic field. The corresponding absorption coefficients of samples are obtained by a fast Fourier transform, and the orientation characteristics of n-alkanes are analyzed under a relative weak magnetic field. The results indicate THz-TDS has great potential for the identification of intermolecular interaction in the organic molecules.

**Keywords:** Magnetic, Molecular, Interaction, Alkanes, Terahertz

**Doi:**

## 1. Introduction

Normal alkanes (n-alkanes),  $C_nH_{2n+2}$ , are among the most basic organic molecules and are building blocks of many other materials including surfactants and polymers, and are themselves the main component of petroleum paraffin, while the properties of alkanes have been known for a long time. New and unexpected phenomena with respect to structural and diamagnetic anisotropy properties continue to be discovered. Magnetic fields are used to align phospholipids, where the alkyl chains play a more significant role [1]. The interaction of the magnetic fields with alkanes themselves and derivative molecules are also of current interest in the petroleum industry.

In recent years, considerable attention has been paid to the degradation of related petroleum products by magnetic methods [2-5]. The effect of a magnetic field on the viscosity of related petroleum oil is very controversial and the controversy was simplified to two aspects. Several researchers have determined that the viscosity of paraffin-based crude oil increases after exposure to a strong magnetic field at 1.5 *T* for an extended time [4]. In contrast, other studies have found that a magnetic field pulse at 0.38 *T* can effectively reduce its viscosity for several hours [2, 3]. Despite the complex paraffin or asphaltene base LBO composition, hydrocarbons with molecular weights in the 250-1000 range dominate all LBOs and can be further subdivided into alkanes, alkenes, alicyclics and aromatics.

Therefore, the fundamental importance of the alkanes makes the detailed characterization and understanding of their behavior a priority. A few studies have been reported on the orientation of alkanes in a magnetic field [6-8]. Paraffin aligns in magnetic field (9 *T*) during crystallization from melt, forming crystallites oriented with respect to the magnetic field [6]. It is found that the long axis of the *n*-alkanes single crystals always aligns perpendicular to the magnetic field and the carbon backbone plane tends to be perpendicular to the field [7]. Apart from these studies, to our knowledge, no work studying the effects of the magnetic treatment of liquid alkanes has been performed to date, and the interaction between the magnetic fields and organic compounds needs further study.

These molecular motion and interaction in liquids and liquid mixtures fall into the THz range [9]. Terahertz time-domain spectroscopy (THz-TDS) has recently received great attention with the expectation that it will provide new insights into complex polymer systems (such as order-disorder transition of nonadecane, higher order conformation, assignment of intermolecular vibration modes and structural characterization, characterizing polymorphism and crystal transformation of polylactide, etc.), and several relevant studies have been reported [10-12]. In this paper, the magnetic field dependence of the THz optical properties are experimentally characterized using THz-TDS. From the measured absorption coefficient  $\alpha$  in the 0.2-2.3 *THz* region, the molecular interaction of *n*-alkanes under a magnetic field is analyzed and identified.

## 2. Experimental section

The commercial liquid *n*-alkanes, such as *n*-pentane (C<sub>5</sub>H<sub>12</sub>), *n*-octane (C<sub>8</sub>H<sub>18</sub>), *n*-decane (C<sub>10</sub>H<sub>22</sub>), *n*-tetradecane (C<sub>14</sub>H<sub>30</sub>) and *n*-pentadecane (C<sub>15</sub>H<sub>32</sub>), at a specified purity of better than 99%, are used without further purification. The THz-TDS measurement performed in a

transmission geometry, which is described in the literature [3]. For the magnetic treatment, without removing the magnets in the process of testing, this paper implements in situ detection of liquid n-alkanes under magnetic treatment. While taking into account the shape of the liquid cell measurement, rectangular permanent magnets are used in parallel experiments as much of the cell surface is covered. A set of permanent magnets are fixed on both sides of the sample cell and two groups of magnet are selected with different magnetic flux densities  $B$  ( $B=14$  and  $34$  mT). Permanent magnets with different thickness are used in order to vary the magnetic field  $B$ .

The color of the samples after magnetic treatments shows no significant difference. The empty cell with a magnetic field is tested first as the reference signal, and liquid sample is injected in the cell and laid aside for 3 min. Then, the THz spectroscopy is measured within 2 min. By comparison with reference and sample pulse, and use of a numerical fast Fourier transform, the refractive index and the absorption coefficient of the samples are calculated. The samples are measured at ambient temperature in a dry nitrogen atmosphere at 20 °C, and the humidity is maintained at less than 1%.

### 3. Results and discussions

The THz pulse waveforms transmitted through the empty cell are displayed in Fig. 1(a) with selected magnetic flux densities ( $B=0, 14, 34$  mT), which are called as the reference pulses. It is clear that the maximum amplitude  $A_s$  is about 0.147 V and slightly dependent upon  $B$ . Fig. 1(a) shows the THz time-domain spectra of  $C_5H_{12}$  in the sample cell under different magnetic flux densities, representing typical experimental results. Fig. 1(c) shows the THz waveforms, measured in transmission, on the original alkanes. The shift of the  $A_s$  to longer time delays with increasing carbon numbers reflects the carbon number dependence of the refractive index. Then, we exact the delay as a function of chain length, at several selected magnetic flux densities. This result is shown in Fig. 1(d), along with a nearly linear fit and nearly  $B$ -independent. These results can be understood by using the well-known Lorentz-Lorentz formula, which relates the refractive index of a liquid to its carbon number [12]. Following Scaife, the refractive index for a given chain length should contain two contributions, such as methylene groups and the two methy end-groups.

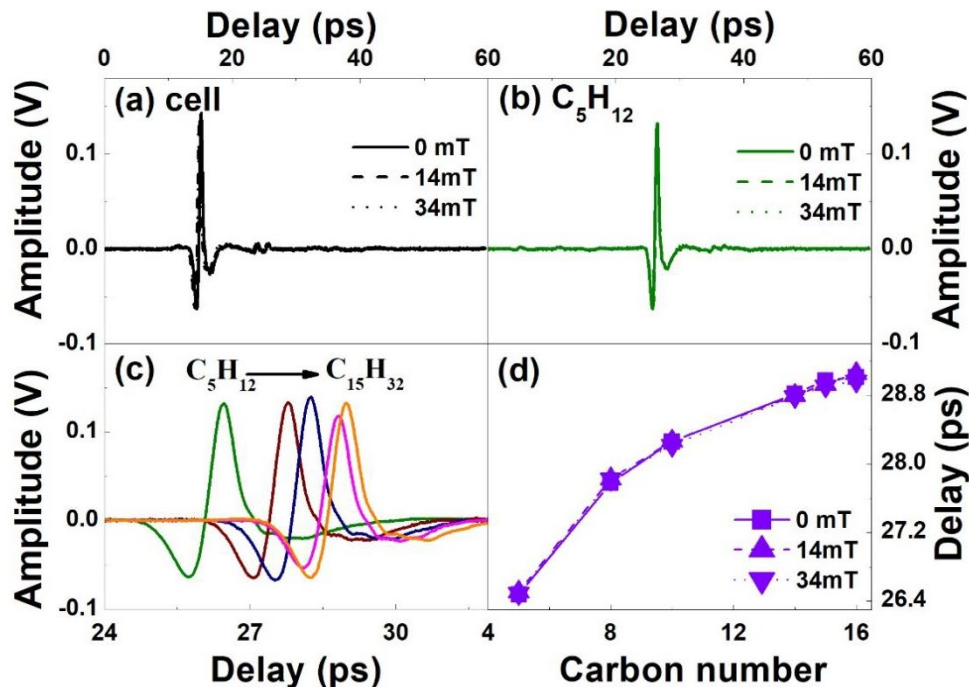


Fig. 1 Time-domain spectra of the terahertz wave transmitted through the (a) empty cell and (b)  $C_5H_{12}$  sample under selected magnetic flux densities  $B$ . (c) The time-domain spectra of the terahertz wave transmitted through the original alkanes. (d) The delay of the alkanes vs. the number of carbon atoms at selected magnetic flux densities  $B$ .

Fig. 2 shows the measured absorption spectra for each of the n-alkanes in the 0.2-2.3 THz region. It is noticed that the original n-alkanes has no obvious sharp absorption peaks in the 0.2-2.0 THz region, but rather shows a monotonic increase with the increasing frequency. However, the original n-alkanes can be identified by their weak absorption peak at approximately 2.2 THz. The absorption of electromagnetic radiation at different frequency ranges corresponds to different physical processes and reveals information about those processes. The vibrational modes of  $C_5H_{12}$ - $C_{10}H_{22}$  are composed of three types in the 0.2-5.5 THz region, namely, skeleton vibration of carbon-carbon (C-C) chain in the yoz plane, swing vibration of C-C chain in the xoy plane, and torsional vibration of methyl group along the y axis [13]. Previously, the absorption peak at 2.2 THz has been obtained in the THz-TDS of n-paraffin crystals ( $C_{19}H_{40}$ ,  $C_{27}H_{56}$ ,  $C_{29}H_{60}$ ,  $C_{30}H_{62}$ , and  $C_{36}H_{74}$ ), liquid paraffin, lube base oils, lubricating oils and many other substances [10-12, 14-16]. Thus, based on these literatures, the recorded 2.2 THz assigned to the  $B_{1u}$  mode, corresponds to the intermolecular interaction between the parallel alkane molecules [10, 17].

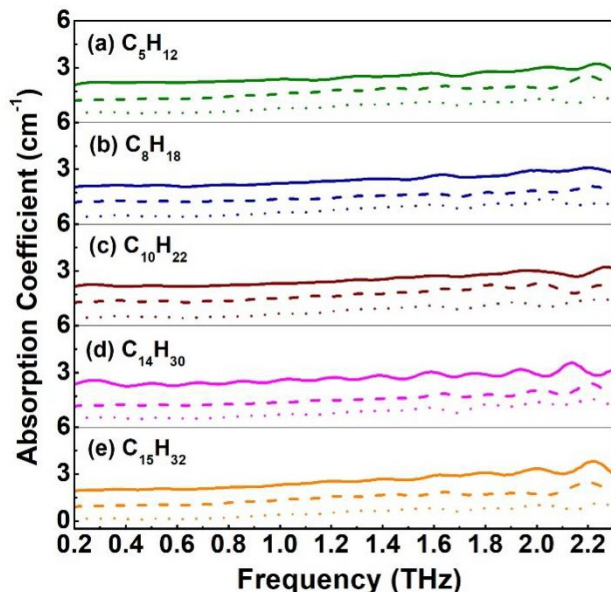


Fig. 2 The absorption coefficients for each of the alkanes at 0 (solid lines), 14 (dashed lines) and 34 mT (dotted lines) from 0.2 THz to 2.3 THz. The y-axis values have been offset to clarify.

We are conducting a further in-depth study with the hope to accurately confirm the effect of magnetization on the intermolecular force in alkanes by THz-TDS. As shown in Fig. 2, the absorption peak for all samples do not shift, but the absorption coefficients decreases in the spectral range. According to the literature, generally, intensity changes due to molecular interactions are observed as a peak shift in the intramolecular vibrations. On the other hand, the molecular interaction intensity changes are observed as the generation and disappearance of peaks and/or the intensity changes in the peaks of direct intermolecular vibrations in the THz frequency region [18].

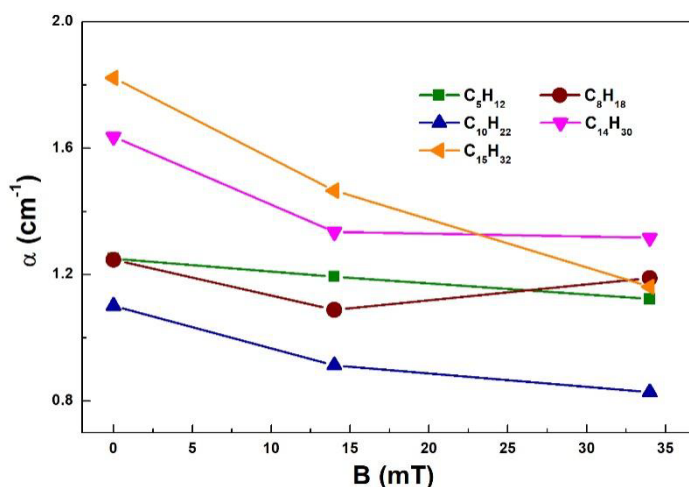


Fig. 3 The absorption coefficients  $\alpha$  for each of n-alkanes versus the magnetic flux densities  $B$ .

The outstanding spectral stability of the measurements allows us to carry out quantitative

analysis. The absorption peak at 2.2 THz corresponding to the intermolecular force is selected as marker bands to illustrate the interaction mechanism between the magnetic field and alkanes molecules by comparing the absorption peak before and after the magnetic treatment. As shown in Fig. 3, the  $\alpha$  at 2.2 THz decreases with the increasing magnetic flux densities, which suggests that the reduction in the intermolecular forces between alkane molecules exists.

As shown in Fig. 4(a), the  $\Delta\alpha$  values located at 2.2 THz, defined as  $\alpha - \alpha_0$ , are all above zero and have nearly linear to the carbon number under both 14 and 34 mT. These results are in excellent agreement with literature [19],

$$\alpha = \sigma_{abs} \cdot \rho N_C / M \quad (1)$$

where  $\sigma_{abs}$  is an effective absorption cross-section for each chain length. By employing the theoretical and experimental diamagnetic susceptibilities of the alkane molecules obtained from the literature, in terms of  $10^{-6}$  cgs units, as a function of the carbon atom number [20-23]. The linearity of the results is shown in Fig. 4(b).

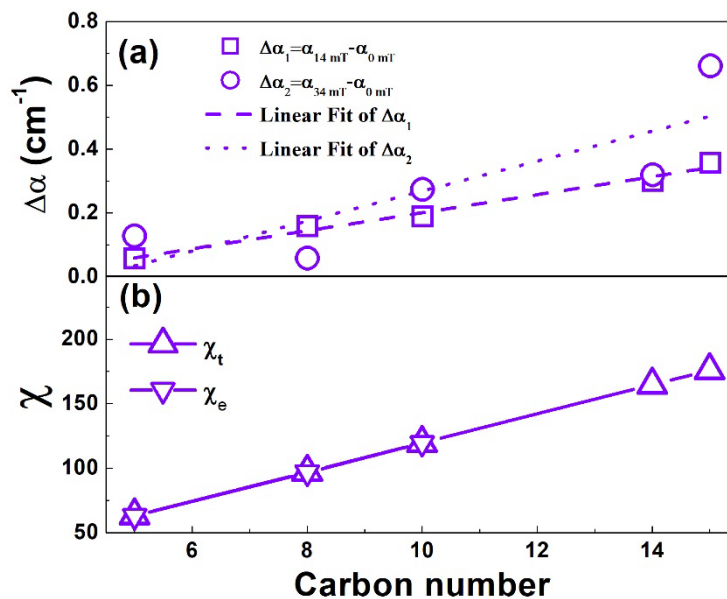


Fig. 4 (a) Difference  $\Delta\alpha$  values, defined as  $\alpha - \alpha_0$ , versus carbon number under  $B=14$  and 34 mT. (b) The theoretical diamagnetic susceptibilities ( $\chi_t$ ) and experimental ones ( $\chi_e$ ) obtained from the References [20-23] and expressed in terms of  $10^{-6}$  cgs units, vs. the number of carbon atoms.

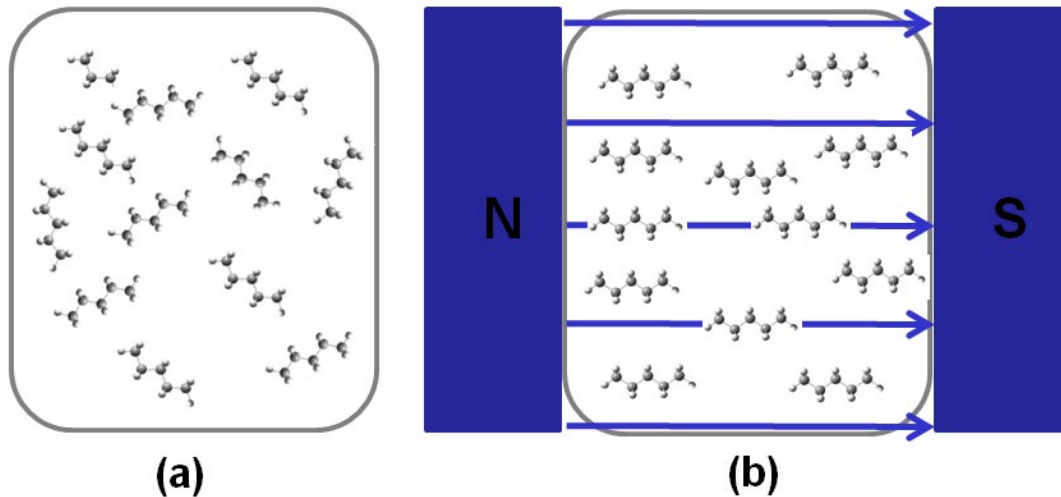


Fig. 5 Schematic illustrations of (a) the vibrating  $C_5H_{12}$  molecules in the field-free space, and (b) the parallel configuration of  $C_5H_{12}$  molecules in the presence of magnetic field.

It is found that the molecular susceptibilities are obtained as sum of contributions from the 1s electrons of carbon atoms, from the various C-C and C-H bonds, and from interactions between various pairs of adjacent C-C and C-H bonds [20]. It is possible to express the theory in a semi-empirical form so that all susceptibilities of the alkane molecules are expressed in terms of three parameters,

$$\chi_i = N_C \chi_C + N_{CC} \chi_{CC} + N_{CH} \chi_{CH} - N_{CC;CC} \chi_{CC;CC} - N_{CC;CH} \chi_{CC;CH} - N_{CH;CH} \chi_{CH;CH} \quad (2)$$

where  $N_C$  is the number of C atoms,  $N_{CC}$  the number of C-C bonds,  $N_{CH}$  the number of C-H bonds,  $N_{CC;CC}$  the number of pairs of adjacent C-C bonds, and  $N_{CC;CH}$  the number of pairs of adjacent C-H bonds. These results are in excellent agreement with literature [19-21], showing that this simple additive model applies even to the longest chains that remain liquid at temperature.

Taking  $C_5H_{12}$  as an example, our method is illustrated in Fig. 5, in which the action of a magnetic field is shown. On the left (Fig. 5(a)), the vibration of  $C_5H_{12}$  molecules are in the field free space. As the liquid flows to the right, passing a region with a relative weak magnetic field directed parallel to the flow direction. The induced decreasing intermolecular forces of C-C chains along the field direction, acquiring a reduced  $[\eta]$  and the effective viscosity is significantly reduced. This is similar to the flow of nematic liquid crystal with its molecular alignment parallel to the flow direction and reducing blood viscosity with magnetic fields [22]. Paraffin with high polydispersity alkanes ranging between  $C_{25}$  and  $C_{45}$  also aligns in a magnetic field (9 T) during crystallization from a melt, forming crystallites oriented with respect to the magnetic field [6]. Magnetic fields

have also been used to align polyethylene [23]. Moreover, Miesowicz found that in such a case, the viscosity is minimized [24].

#### 4. Conclusions

In summary, liquid n-alkanes subjected to magnetic field treatments are characterized by THz-TDS, and the absorption coefficient values are obtained. The absorption peak of the original alkanes at approximately 2.2 THz corresponding to intermolecular interactions is selected as marker bands to illustrate the interaction mechanism. A magnetic field induced orientation of the organic molecules is suggested by the decreasing of absorption coefficients with applied magnetic fields. The results obtained in this work demonstrate that THz-TDS is a powerful tool that can provide evidence for the intermolecular interaction of organic molecules.

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#### References

- [1] Isabettni S, Massabni S, Hodzic A, et al. "Molecular engineering of lanthanide ion chelating phospholipids generating assemblies with a switched magnetic susceptibility[J]". *Physical Chemistry Chemical Physics*, 19: 20991-21002 (2017).
- [2] Tao R and Xu X. "Reducing the viscosity of crude oil by pulsed electric or magnetic field[J]". *Energy Fuels*, 20 (5): 2046-2051 (2006).
- [3] Jiang C, Zhao K, Zhao L J, et al. "Probing disaggregation of crude oil in a magnetic field with terahertz time-domain spectroscopy[J]". *Energy Fuels*, 28: 483-487 (2014).
- [4] Chow R, Sawatzky R, Henry D, et al. "Precipitation of wax from crude oil under the influence of a magnetic field[J]". *Journal of Canadian Petroleum Technology*, 39 (6): 56-61 (2000).
- [5] Schmelcher P. "Molecule formation in ultrahigh magnetic fields[J]". *Science*, 337 (6092): 302-303 (2012).



- [6] Kimura T, Yamato M, Koshimizu W, et al. "Magnetic-field induced orientation of paraffin[J]". *Chemical Letters*, 28: 1057-1058 (1999).
- [7] Shao H H, Gang H and Sirota E B. "Magnetic-field induced orientation and anisotropic susceptibility of normal alkanes[J]". *Physical Review E*, 57: R6265 (1998).
- [8] Schreiner P R, Chernish L V, Gunchenko P A, et al. "Overcoming lability of extremely long alkane carbon-carbon bonds through dispersion forces[J]". *Nature*, 477: 308 (2011).
- [9] Tian R H, Bao R M and Tian L. "Probing the liquid-solid transition of petroleum macromolecules with terahertz time-domain spectroscopy[J]". *Science China Physics, Mechanics & Astronomy*, 61: 104221 (2018).
- [10] Tanno T, Asari J, Yodokawa S, et al. "Terahertz spectroscopic study on order-disorder phase transition of nonadecane[J]". *Chemical Physics*, 461: 25-28 (2015).
- [11] Tian L and Xu X L. "Optical properties and crystallization of natural waxes at several annealing temperatures: a terahertz time-domain spectroscopy study[J]". *Journal of Infrared, Millimeter and Terahertz Waves*, 39: 302-312 (2018).
- [12] Tian L and Ni H. "Sonochemical degradation of various lubricating oils investigated using terahertz time-domain spectroscopy[J]". *Optik*, 208: 164054 (2020).
- [13] Tian L and Ni H. "The vibrational dynamics of n-alkanes in the terahertz region[J]". *Science China Physics, Mechanics & Astronomy*, 45: 084205 (2015).
- [14] Tian L and Ni H. "Effects of ultrasonic irradiation on the upgradation of lube base oil investigated using terahertz time-domain spectroscopy[J]". *Vibrational Spectroscopy*, 114: 103254 (2021).
- [15] Srivastava S P, Handoo J, Agrawal K M, et al. "Phase-transition studies in n-alkanes and petroleum-related waxes-a review[J]". *Journal of Physics and Chemistry of Solids*, 54: 639-670 (1993).
- [16] Laib J P, Nickel D V and Mittleman D M. "Terahertz vibrational modes induced by heterogeneous nucleation in n-alkanes[J]". *Chemical Physics Letters*, 493: 279-282 (2010).
- [17] Williams S D, Johnson T J, Sharpe S W, et al. "Quantitative vapor-phase IR intensities and DFT computations to predict absolute IR spectra based on molecular structure: I. Alkanes[J]". *Journal of Quantitative Spectroscopy and Radiative Transfer*, 129: 298-307 (2013).
- [18] Nagai N, Kumazawa R and Fukasawa R. "Direct evidence of inter-molecular vibrations by THz spectroscopy[J]". *Chemical Physics Letters*, 413: 495-500 (2005).
- [19] Laib J P, Nickel D V and Mittleman D M. "Temperature-dependent terahertz spectroscopy of liquid n-alkanes[J]". *Chemical Physics Letters*, 493: 279-282 (2010).
- [20] Hameka H F. "Theory of the diamagnetic susceptibilities of the alkanes[J]". *The Journal of Chemical Physics*, 34: 1996 (1961).

- [21] Broersma S. "The Magnetic Susceptibility of Organic Compounds[J]". *The Journal of Chemical Physics*, 17: 873 (1949).
- [22] Tao R and Huang K. "Reducing blood viscosity with magnetic fields[J]". *Physical Review E*, 84(1): 011905 (2011).
- [23] Nagai N, Ishikawa G, Noguchi K, Takahashi K, et al. "Magnetic-field induced alignment of low molecular weight polyethylene[J]". *Polymer*, 54 (2): 784-790 (2013).
- [24] Miesowicz M. "The three coefficients of viscosity of anisotropic liquids[J]". *Nature*, 158: 27 (1946).