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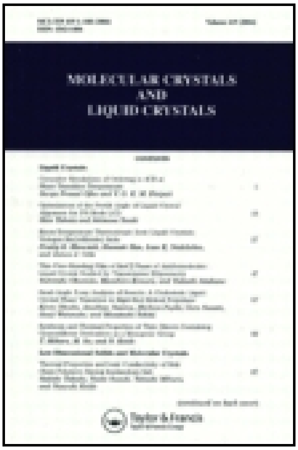

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A Universal Behavior for the Ratio between the Miesowicz's Coefficients for Rigid Calamitic Molecules of Nematic Liquid Crystals

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A Universal Behavior for the Ratio between the Miesowicz's Coefficients for Rigid Calamitic Molecules of Nematic Liquid Crystals

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In this work a geometrical interpretation to the ratio between the Miesowicz's coefficients will be proposed. We will show that the thermodynamic parameters describing the viscosity coefficients can be separated in two classes; those describing the orientation of the molecules, and those describing their overall behavior. This fact suggests that the ratio between any two of the Miesowicz's coefficients have a universal behavior that is dominated by the geometric orientation of the long axis of the molecules of the material during the shear flow. In order to inspect this hypothesis, the kinetic results for the viscosity's coefficients have been studied and it is shown that this theory is in accord with a universal behavior for the ratio between the Miesowicz's coefficients. Nevertheless, the experimental data does not agree with the prediction of these calculations.

Keywords: Rheology; Viscosity; Miesowicz's coefficients

INTRODUCTION

Anisotropy is a basic characteristic of the liquid crystal (LC) state[1]. Many of its thermodynamic properties are direction dependent and, certainly, the characteristic anisotropy form of its molecules is the responsible for its macroscopic anisotropy. There are, for example, some successful models that link the difference between the elastic constants with the relative dimensions

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these three directions Miesowicz defined the now called Miesowicz's viscosity coefficients, where

η_1 gives the viscosity when the magnetic field is parallel to the gradient of the velocity,

η_2 gives the viscosity when the magnetic field is parallel to the direction of the flow,

η_3 gives the viscosity when the magnetic field is perpendicular to the direction of the flow and also perpendicular to the velocity gradient.

These viscosity's coefficients take care of the shearing motion of the liquid on the sample. The nematic liquid crystals have other two independent viscosity's coefficients related with the rotations of the nematic domains[1]. In this paper we will only consider the Miesowicz's coefficients.

We will begin this section by making some thermodynamic considerations about the general form of the Miesowicz's coefficients. The aim of these ideas is to grasp the physical meaning of the ratio between the Miesowicz's coefficients. The main ingredient that will be used on it is the Miesowicz's discovery that to change the viscosity of the nematic liquid crystal it is enough to change the direction of the external magnetic field. Hence, consider a large sample, with dimensions (a, b, d), in which any surface's influence can be disregarded. Suppose that the nematic fluid is flowing along the $\vec{e}_x$ direction and that its velocity depends only on the position along $\vec{e}_z$. So, we may consider that the fluid motion is composed of sheets of constant velocity and, as we move along $\vec{e}_z$, a new sheet with a different velocity is found at each z position. Now on, we will call these sheets by shear planes. For simplicity, suppose that the velocity increases continuously as we move up along the $\vec{e}_z$ direction. Hence, if we consider a given sheet, there will be another sheet below it that will try to put it in a small velocity and another one upon it that will try to put it in a bigger velocity. Therefore, the molecules of one sheet interact with the other ones in the neighbor sheets and push, or pull, them trying to change its momentum. By definition, the viscosity arises in the transport of momentum between these different sheets[18, 19] and, consequently, it must depend on the relative orientation between the molecules at adjacent moving sheets. In terms of the orientation of the molecules we can reinterpret the Miesowicz's discovery by saying that when the orientation of the molecules on the shear plane is changed, the interaction between the planes that are above and below it also changes. This change of orientation is a geometrical change and, therefore, this is the physical origin of the change of the viscosity. Hence, for each of the three different perpendicular geometrical orientations of the director, three different viscosity's parameters have been measured. Furthermore, the viscosity of a nematic material can be changed with the sole change of the orientation between the molecule long axis and the shear plane, and no other thermodynamical variable is evolved. Below we will

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of the nematic molecules[2]. But the same does not happen with the coefficients of viscosity. It is known from long ago that the flow of these materials, in the presence of an external field, may depend on the relative direction between an external field and the gradient of the velocity on the fluid[3, 4]. The main hydrodynamic approach to these LC's peculiar properties is due to Ericksen, Leslie and Parodi (ELP approach)[5, 6, 7, 8, 9, 10]. This treatment assumes that the LC is a continuo in which the viscosity tensor is written as the most general structure combining the director field, the symmetric part of the velocity gradient, and the vector giving the time rate of the change of the director's direction. The six coefficients, combining these terms, are known as Leslie's viscosity coefficients and, according to the ELP approach, they must be determined by the experiment. Furthermore, using a time inversion argument of Onsager[11], Parodi[7] had shown that these six coefficients could be reduced to five independent ones.

As the experimental determination of the Leslie coefficients is not an easy task, a great effort has been done for their calculation from a microscopic point of view. The use of the kinetic equations[12, 13, 14, 15, 16, 17] for the determination of these coefficients has current and widespread practice. Nevertheless, as it will be shown ahead, these calculations can not explain some observed ratio between the Miesowicz's coefficients.

We will begin this work presenting some general thermodynamic arguments showing that the ratios between the Miesowicz's coefficients of rigid molecules must follow a universal relationship. We will show that geometrical contribution due to the shape of the molecules of the nematic liquid can be factorized from the Miesowicz's coefficient. So, it will be concluded, compounds having molecules with proportional dimensions may have proportional viscosity's coefficients. Afterwards, we will show that the molecular kinetic calculations of the Miesowicz's coefficients also predict a similar relations between the Miesowicz's coefficients. But, on these relations, the geometrical meaning of such universal relation is not clear and the curve that it predicts does not agree with the experimental results.

FUNDAMENTALS

In 1935 M. Miesowicz reported the existence of modifications in the viscosity of the PAA when the direction of an external magnetic field is changed. [3, 4]. He has shown that these variations on the observed viscosity is determined by the relative orientation between the orientation of the long axis of the nematic molecule and two other directions describing the shear plane: the direction of the fluid flow and the direction of the velocity fluid gradient. Using the relative orientation of

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use this observation to construct a general form to the ratio between the Miesowicz's coefficients.

Let us assume that the Miesowicz's viscosity coefficients are thermodynamic variables that admit a separation between the parameters describing their overall behavior and the parameters describing the mean orientation of the long axes of the rod-like molecule. In order to understand this hypothesis, let us consider that the Miesowicz's viscosity coefficients are function of the number of micelles in a unit volume ϱ, the random thermal motion of its center of mass T, the order parameter S describing the mean ordered orientation of the nematic domains, and the mean relative orientation between the molecular long axes and the shear plane, here generically represented by the variable σ_i $(i = 1, 2, 3)$. Hence,

$$\eta_i = \eta(\varrho, T, S, \sigma_i), \qquad i = 1, 2, 3. \tag{0.1}$$

Observe that the variables ϱ, T and S are connected with the overall thermodynamical behavior of the molecules, and do not change when the mean relative orientation σ_i is changed. Furthermore, according to the preceding discussion, the viscosity η_i can be changed with the sole change of the mean relative orientation of the molecules σ_i, without any change in the variables ϱ, T and S. Therefore, the function η_i may admit the factorization

$$\eta_i = f(\varrho, T, S)\ g(\sigma_i), \qquad i = 1, 2, 3 \tag{0.2}$$

where $f(\varrho, T, S)$ accounts for the contribution of ϱ, T, S, and $g(\sigma_i)$ is a function restricted to description of the physical properties of the mean relative orientation of the molecule and the shear plane. However, the function σ_i can not be considered as an independent one. That is, as it describes a relative mean orientation it must depend, for example, the order parameter S (which also describes the orientational fluctuation of the aligned molecules). For instance, when the nematic-isotropic (N-I) phase transition is approached we would expect that $\eta_i/\eta_j \to 1$, because, at this region, the rotational fluctuations of the long axis of the molecule around the director direction must make irrelevant any geometrical difference between the Miesowicz's configurations.

From the above equation, it follows that the ratio between any two viscosity coefficients

$$\frac{\eta_i}{\eta_j} = \frac{g(\sigma_i(S))}{g(\sigma_j(S))}, \tag{0.3}$$

is dominated by the relative geometrical character of the orientations represented by $g(\sigma_i)$ and $g(\sigma_j)$.

In order to show that the above relation leads to an universal relation to the ratio between the Miesowicz's coefficients let us remember that the Maier and Saupe[20, 1] formulation of the

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N-I phase transitions implies that the order parameter S would have a universal behavior when the temperature is measured in terms of the N-I critical temperature. So, using such temperature scale, we can expect that for those compounds for which the relative dimensions of its molecules are proportional the curves obtained with the ratio of Eq. (0.3) would lie approximately along the same line.

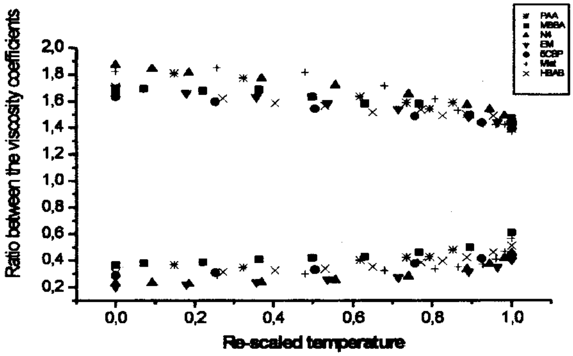

Figure 1- Experimental data showing the values of η_3/η_2 and η_3/η_1. The set of data points at the upper part of the picture shows the values of η_3/η_2. There is a strong coincidence among the temperature dependence of these ratios and, furthermore, they seem to converge, in the limit of low temperatures, to 1.7. The set of data points at the basis of the picture shows the values of η_3/η_1. The experimental values of these ratio fluctuate around the value 0.3. We have collected these viscosity data curves of LC from Refs. [21, 22, 23, 24, 25, 26, 27]. The continuous lines were obtained using the mean of the values exhibited in the tables 1 and 2. Experimental data were re-scaled in such a way that the nematic isotropic transition would correspond to the point $T = 1$, and the nematic-crystalline point correspond to $T = 0$.

To compare these predictions with experimental results, we have collected viscosity data points of liquid crystals from the Refs.[21, 22, 23, 24, 25, 26, 27]. The temperature was re-scaled in such a way that the nematic isotropic transition correspond to the point $T = 1$, and the nematic-crystalline point correspond to $T = 0$. The experimental results are shown in fig. 1. From this

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figure, we see that, as have been anticipated, the sets of points corresponding to η_3/η_1 and η_3/η_2 are not random distributed. They occupy two distinct regions, indicating the existence of a single general pattern for each ratio, and suggesting the existence of a unique line along which each of these ratios are distributed. The values of η_3/η_1 fluctuate around $\eta_3/\eta_1 \sim 0.3$, having a small increasing with the temperature. The values of η_3/η_2 fluctuate around $\eta_3/\eta_1 \sim 1.7$, having a small decreasing with the temperature. Furthermore, as expected, both curves seem approach 1 as the temperature approaches the N-I transition. The regularity and agreement observed in these experimental data is astonishing. After a simple re-scaling in the temperature, the ratios between the Miesowicz's coefficients of distinct compounds, for which the absolute values of the viscosity are totally different, are distributed along two coinciding curves, suggesting the existence of a universal behavior.

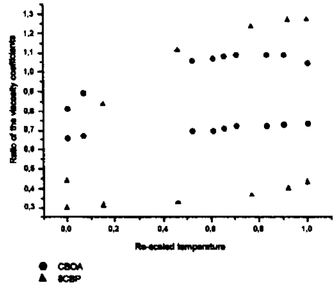

Figure 2- Experimental data, obtained from Refs.[21, 24], showing the values of η_3/η_2 and η_3/η_1 for CBOA and 8CBP. The data for η_3/η_2 are represented using down triangles, and the data for η_3/η_1 are represented using up triangles. For these materials the ratio between the Miesowicz's coefficients do not follow the same curves obtained in the fig. 1. As it is known, they are not rigid calamitic compounds, and there is a change in the form of these compounds during a temperature variation. So, we can conclude that the responsible for the universality suggested by in the data in the fig.1 may be the constant calamitic form of those material.

In order to verify if there are further experimental evidences that the constancy between the geometric proportions of the rod-like molecules are the responsible for the "universal" lines found

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above, we look for experimental viscosity data of compounds that do not preserve the rod-like proportions during the change of temperature. There are at lest two compounds, with known Miesowicz's coefficients, exhibiting this property. They are the 8CBP[21] and the CBOA[24]. In fig. (2) the data for the ratio between their Miesowicz's coefficients is shown. As expected, these data do not follow the general trends of the fig. (1), and this difference can be attributed to the temperature dependence of the form of these materials. Of course, this result does not prove that the geometrical origin of the "universality" of the curves exhibited in fig. (1). But, surely, it is a strong evidence of this fact.

THE KINECTIC APPROACH

The results of the last section follow from general considerations about the nature of the anisotropic viscosity, and do not give a computable expression to the function $g(\sigma_i)$. So, the present form of the Eq.(0.3) only indicates the existence of a relation between the anisotropic viscosity and the molecular geometry. In order to produce an expression to $g(\sigma_i)$ a model for the viscosity must be introduced and, in order to evaluate its confidence, comparisons with experimental data must be done. These two tasks will be done ahead. In this section an expression to the Eq.(0.3) that follows from the molecular kinetic theory will be presented and, in the sequence, it will be compared with experimental results.

There are some molecular predictions for the values of the viscosity's coefficients based on the molecular approach that follows from the Smoluchowski equation. Here, the results found by M. Doi and N. Kuzzu, and improved by Larson, will be used[14, 28, 29]. Similar expressions have been found by other researches[12, 15, 16]. Using the kinetic results of R.G. Larson[28, 29] for the Leslie coefficients, we have found that the corresponding Miesowicz's viscosity coefficients may be written as

$$\eta_1 = \frac{\mathrm{n}}{70}\left(21 - 70\,R(p)\,S_2 + \frac{1225\,{S_2}^2}{14+5\,S_2+16\,S_4} + R(p)^2\,(14+5\,S_2+16\,S_4)\right), \qquad (0.4)$$

$$\eta_2 = \frac{\mathrm{n}}{70}\left(21 + 70\,R(p)\,S_2 + \frac{1225\,{S_2}^2}{14+5\,S_2+16\,S_4} + R(p)^2\,(14+5\,S_2+16\,S_4)\right), \qquad (0.5)$$

$$\eta_3 = \frac{\mathrm{n}}{2}\left(0.6 - \frac{2\,R(p)^2\,(-7+5\,S_2+2\,S_4)}{35}\right), \qquad (0.6)$$

where $S_2 = \langle P_2(\vec{u}.\vec{n})\rangle$ and $S_4 = \langle P_4(\vec{u}.\vec{n})\rangle$ are the equilibrium order parameters[1], $P_2(x)$ and $P_4(x)$ are the Legendre's Polynomials, and $\langle x\rangle$ gives the mean value of the random variable x, taken over the equilibrium angular distribution function $f_0(x)$ that, using $x = \vec{u}.\vec{n}$, gives the probability that an arbitrary nematic domain is found in the direction of the unit vector $\vec{u}$, once $\vec{n}$ is unit vector parallel to the average direction of $\vec{u}$. $R(p) = (p^2-1)/(p^2+1)$, where p is the aspect ratio of the spheroid of revolution representing the nematic micelle. Furthermore $n = \varrho K_B T/2\bar{D}_r$, where $\bar{D}_r$ is the rotational diffusion coefficient with depends on the concentration, the molecular weight and the angular distribution function $f_0(x)$.

Using the values of S_2 and S_4 predicted by the Mayer-Saupe theory[20] in these equations the values of the Miesowicz's coefficients can be predicted and compared with experimental values. A good example of how it can be done may be found in the book of R. G. Larson, Chapter 10, fig. (10.9). In this calculation it is shown that there is a generic agreement between the position of the experimental data of the MBBA and the prediction of the theoretical calculation. Therefore, the molecular kinetic theory describes the general trends of the experimental data. But, as will be observed ahead, when the ratio between the Miesowicz's coefficients is considered the details of these curves may become significant and eventually dominate the overall behavior of the curve. In this case the agreement with the experimental results may become not so good.

Furthermore, from these equations we see that the ratios η_3/η_1 and η_3/η_2 are totally determined by the parameters p, S_2 and S_4. That is, the parameter n, that like the function $f(\varrho, T, S)$ of the Eq.(0.2), explicitly displays overall thermodynamic characteristics of each nematic specimen, is not present on these ratios. So, the parameters that appear in the above equation describe some universal property (or properties) of the nematic structure. Indeed, one can affirm that the parameter p can change from one material to another. But, for nematic calamitic molecules that do no have a substancial form variation in all the range of the nematic phase we can say that p does not have a significant change from one nematic specimen to another. So, the ratio between the Miesowicz's coefficients obtained with the kinetic approach seems to confirm the geometrical interpretation that we have given above. Moreover, as we have explained above, if it is assumed that the interaction between the micelles is essentially independent of the temperature T, the order parameters S_2 and S_4 become universal parameters of $t = T/T_{NI}$, where T_{NI} is the temperature of the N-I phase transition[1, 20]. So, it can be concluded that the ration in the Eq.(0.3) must be approximately the same for all the nematics specimens for which the geometric proportions are equivalent.

In order to evaluate the kinetic predictions for the ratio between Miesowicz's coefficients we used the values of S_2 and S_4 calculated from the Maier-Saupe model[20, 28] and, for the

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parameter p, it was used $p = 10$. The result of this calculation is put in fig. (1) as a dashed line, where we see that the general trends and values for these ratios predicted by the molecular theory do not agree with the experimental values. The ration η_3/η_1 can roughly describe the experimental observations. Nevertheless, for η_3/η_2 the curve predicted by the kinetic approach has not the same behavior observed on experimental points. Indeed, for η_3/η_2 the experimental and theoretical curves only agree at $t = 1$, and as the point $t = 0$ is approached the two curves have a striking different behavior. We have done the same calculation using another predictions for the Miesowicz's coefficients done by another authors. We have never found a curve for η_3/η_2 that may, even roughly, explain our findings for η_3/η_2.

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References

[1] P.G. de Gennes, *The Physics of Liquid Crystals*, Clarendon Press, Oxford, 2nd edition, 1993.

[2] J. Nehring, A. Saupe J. Chem. Phys. 54, 337 (1971).

[3] M. Miesowicz. Nature, 136, 261 (1935).

[4] M. Miesowicz. Bull., Acad. Po. A, 228 (1936).

[5] J.L. Ericksen, Arch. Ratl. Mech. Anal. 4, 231 (1960); **9**, 371 (1962).

[6] F.M. Leslie, Quart. J. Mech. Appl. Math. **19** 357 (1966).

[7] O. Parodi, J. Physique (Paris) **31**, 581 (1970).

[8] Foster, D., Lubensky, T., Martin, P., Swift, J., and Pershan, P. Phys. Lett. 26, 1016 (1971).

[9] Martin, P.C., Parodi, O., and Pershan, P. Phys. Rev. A6, 2401 (1972).

[10] Martin, P.C., Pershan, P.J. Swift, J. Phys. Rev. Lett. 25, 844 (1970).

[11] Onsager, L. *Phys. Rev.* **37**, 405 (1931). Onsager, L. *Phys. Rev.* **38**, 2265 (1931).

[12] M.A. Osipov, E.M. Terentjev, *Z Naturforsch* 44a 785 (1989), *Mol. Cryst. Liq. Cryst.* 198 428(1990), *Il Nuovo Cimento* 12 1223 (1990).

[13] Doi, M., Edwards, F., J.C.S. Faraday **74** 918 (1978).

[14] Kuzuu, N., Doi, M., *J. of Phys. Soc. of Japan* 52 3486 (1983). *J. of Phys. Soc. of Japan* 53 1031 (1984).

[15] Marrucci, G., *Mol. Cryst. Liq. Cryst.* **72** (Letters) 153 (1982).

[16] Kikpatric, T.R. *J. Chem. Phys.* **89**(8) 5020 (1988).

[17] Doi, M., Edwards, S.F., *The Theory of Polymer Dynamics*; Oxford Press, New York, 1986.

[18] Reif, F., *Fundamentals of Statistical and Thermal Physics.* Mcgraw-Hill Kogakusha, Ltda Tokio, Japan (1965).

[19] Huang, K., *Statistical Mechanics*, John Wiley & Sons, Inc., New York (1963).

[20] Maier, W., Saupe, A., Z. Naturforsch **A13**, 564 (1958); **A14**, 882 (1959); **A15**, 287 (1960).

[21] H. Kneppe, F. Scheneider, N.K. Sharma, Ber. Bunsenges Phys. Chem. **85**, 784–789 (1981).

[22] C.H. Gahwiller, Mol. Cryst. Liq. Cryst. **20**, 301 (1972).

[23] W.H. de Jeu, W.A.P. Claassen, A.M.J. Spruijt, Mol. Cryst. Liq. Cryst. **37**, 269 (1976).

[24] M.G. Kim, S. Park, Sr. M. Cooper, S.V. Letcher, Mol. Cryst. Liq. Cryst. **36**, 143 (1976).

[25] N.V. Madhsudana, P.P. Karat, S. Shandrasekhar. Pranama Suppl. **1**, 225 (1975).

[26] G.P. Chen, H. Takezoe, A. Fukuda. Liquid Crystal, **5**, 347 (1989).
[27] Chmiclcwski, Mol. Cryst. Liq. Cryst. **132** 339 (1986).
[28] Larson, R.C., Archer L.A., Liquid Cristals **19**, 883 (1995).
[29] Larson, R.G., *The structure and Rheology of Complex Fluids.* Oxfor University Press, 1999.

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