

Geometric approach to the Miesowicz coefficients at the region of the crystalline-nematic transition and a universal relation for their ratio

M. Simões and S. M. Domiciano

Departamento de Física, Universidade Estadual de Londrina, Campus Universitario, 86051-970, Londrina (PR), Brazil

(Received 9 March 2002; published 16 December 2002)

In this work the ratios between the Miesowicz coefficients of rigid calamitic nematic liquid crystals will be studied. It will be shown that the microscopic theory that describes these coefficients, the kinetic theory [M. Doi and S. F. Edwards, *The Theory of Polymer Dynamics* (Oxford Press, New York, 1986)], suggests that some ratios between the Miesowicz coefficients would have a universal character, that does not depend on the nematic material being examined. A set of experimental data has been collected from the liquid crystal literature and, once these data are rescaled in a common temperature scale, they point to the existence of such a universality. Nevertheless, only in the neighborhoods of the nematic-isotropic transition, do the theoretical calculations of the kinetic theory and the experimental data predict the same profile for this universality; when the region of the crystalline-nematic transition is approached theory and experiment present severe discrepancies. The reason for this disagreement is studied and it is proposed that it results from the fact that the kinetic theory does not take into account the packing properties of the nematic medium. A different approach to the calculation of these ratios is proposed and it is shown that it describes the experimental data for all temperatures.

DOI: 10.1103/PhysRevE.66.061703

PACS number(s): 61.30.Gd, 61.30.Jf, 64.70.Md

I. INTRODUCTION

In 1935 [1,2], it was established that in the presence of external fields some liquid crystal (LC) materials could present anisotropic viscosity, i.e., the measured value of the viscosity depends on the relative direction between an external field and the shearing plane. Nowadays, it is known that this phenomenon has an origin in the anisotropic shape of the nematic domains; as the direction of the external field is changed the collective mean orientation of these molecules with relation to the shearing plane also changes, establishing different physical conditions to the transport of momentum between the adjacent shearing planes. The prototype theory, whose phenomenological results all microscopic models must explain is the ELP approach [3–8], which, starting from hydrodynamics considerations, shows that on these materials the dissipation due to fluid flow must be characterized by five different viscosity coefficients. Three of them describe the three different possibilities for the relative orientation between external field and the shearing plane, known as Miesowicz's coefficients. The other two describe the symmetric and the antisymmetric combinations of the shearing around a nematic domain, the rotational coefficients. There are few theories that, starting from microscopic considerations, try to explain these results. The most known one is the so-called kinetic theory [9]. This theory, originally formulated for polymers and extended for LCs [9–14], is able to give a microscopic explanation to the observed anisotropy on the LC viscosity coefficients but, as will be shown ahead, some universal relations [15] between these coefficients cannot be correctly explained by it.

In Sec. II it will be shown that an immediate consequence of the kinetic theory [16,17] is the fact that the ratio between the Miesowicz coefficients of rigid calamitic molecules would present a universal behavior that does not depend on

the particular nematic material being examined. In Sec. III it will be shown that for a broad set of nematic materials the experimental results are in agreement with the existence of such universality, but the observed values of these data do not agree with the predictions of the kinetic theory. It will be argued that the reason of such disagreement is that the kinetic approach does not consider the geometric properties of the packing of the nematic domains, which become important when the crystalline-nematic transition point is approached. In Sec. IV a definition of stress tensor that emphasizes the role of the nematic packing [9] is used to make an evaluation of the Miesowicz coefficients that confirms the prediction of a universal behavior for these ratios and, with that, the universality observed in the distribution of the experimental data points could be correctly explained. In synthesis, in this work it is shown that the ratio between the Miesowicz coefficients of rigid calamitic nematic liquid crystal presents a universal behavior which can be explained with the geometric properties of the packing of the nematic domains.

II. MIESOWICZ'S COEFFICIENTS AND KINETIC THEORY

The observation of modifications on the viscosity of an LC, when the direction of an externally applied magnetic field is changed, leads to the following definition for the Miesowicz viscosity coefficients:

- (i) η_1 , when the long axis of the molecules is parallel to the gradient of the velocity,
- (ii) η_2 , when the long axis of the molecules is parallel to the direction of the flow,
- (iii) η_3 , when the long axis of the molecules is perpendicular to the direction of the flow and also perpendicular to the velocity gradient.

Figure 1 defines the geometry used along with this work

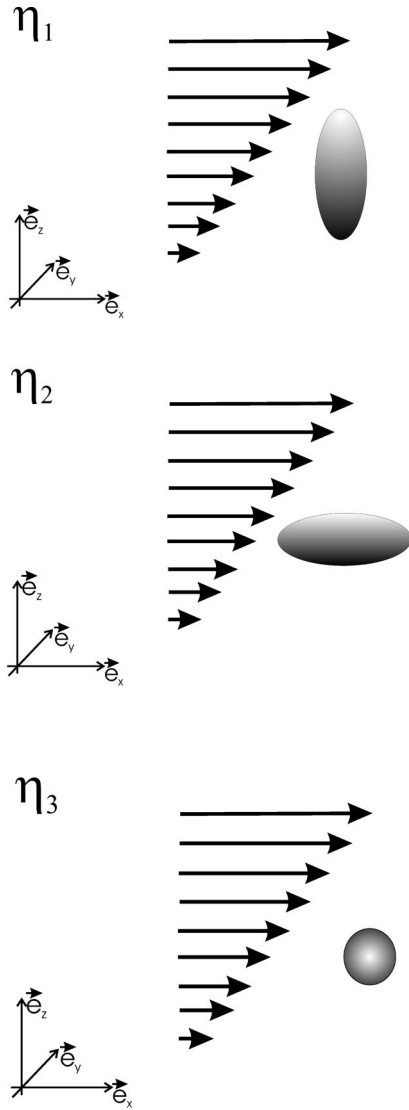


FIG. 1. This figure defines the geometry that is used to calculate each one of the Miesowicz coefficients in this work. The arrows give the direction of the fluid flow and the continuous variation of its length represent the variation of the fluid velocity. For each Miesowicz coefficient the molecular long axis has a different orientation relative to the direction of the fluid flow. In (a) the geometry of the coefficient η_1 is shown, the long axis of the molecules is parallel to the gradient of the velocity. In (b) the geometry of the coefficient η_2 is shown; the long axis of the molecules is parallel to the direction of the flow. In Fig. (c) the geometry of the coefficient η_3 is shown, the long axis of the molecules is perpendicular to the direction of the flow and also perpendicular to the velocity gradient.

and illustrates, for each one of the Miesowicz coefficients, the relative orientation between the direction of the long axis of the nematic domains and the direction of the fluid flow; it will be supposed that the nematic fluid is flowing along the \vec{e}_x axis and that its velocity depends only on the position along the \vec{e}_z axis. So, it may be assumed that the fluid motion is composed of sheets of constant velocity and, as one moves along the \vec{e}_z direction, a new sheet with a different velocity is found. Hence, given a sheet, two other sheets will surround

it; one below that will try to reduce its velocity, and another above that will try to increase its velocity. Now on these sheets will be called by shearing planes. Therefore, the nematic domains in one shearing plane interact with other domains in the neighbor shearing planes trying to change its momentum. By definition, the viscosity arises from the transport of momentum between different shearing planes [18,19] and, as the nematic domains can be orientated, the flux of momentum between these planes depends on this orientation.

There are some predictions for the values of the viscosity's coefficients based on microscopic considerations, the kinetic approach is certainly the most well known [9]. The results found by Doi and Kuzuu, and improved by Larson [12,16,17], will be used here. Similar expressions have been found by other researches [10,13,14]. Using these results we have found that the corresponding Miesowicz coefficients may be written as

$$\begin{aligned} \eta_1 &= \frac{n}{70} \left(21 + 70R(p)S_2 + \frac{1225S_2^2}{14 + 5S_2 + 16S_4} \right. \\ &\quad \left. + R(p)^2(14 + 5S_2 + 16S_4) \right), \\ \eta_2 &= \frac{n}{70} \left(21 - 70R(p)S_2 + \frac{1225S_2^2}{14 + 5S_2 + 16S_4} \right. \\ &\quad \left. + R(p)^2(14 + 5S_2 + 16S_4) \right), \\ \eta_3 &= \frac{1}{2} n \left(0.6 - \frac{2R(p)^2(-7 + 5S_2 + 2S_4)}{35} \right), \end{aligned} \quad (1)$$

where $S_2 = \langle P_2(\vec{u} \cdot \vec{n}) \rangle$ and $S_4 = \langle P_4(\vec{u} \cdot \vec{n}) \rangle$ are the equilibrium order parameters [20], $P_2(x)$ 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 $x = \vec{u} \cdot \vec{n}$, gives the probability of finding an arbitrary nematic domain in the direction of the unit vector \vec{u} , once \vec{n} is a 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 $n = \rho K_B T / 2\bar{D}_r$, where \bar{D}_r is the rotational diffusion coefficient which depends on the concentration, the molecular weight, and the angular distribution function $f_0(x)$.

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 . The unique parameter n that in Eq. (1) could be used to distinguish one nematic material from another is not present on these ratios. That is, the Mayer-Saupe theory predicts that, once assumed that the interaction between the micelles is independent of the temperature T , the order parameters S_2 and S_4 would become universal functions of $t = T/T_{NI}$, where T_{NI} is the temperature of the N-I phase transition [20,21]. Moreover, p is a geometrical parameter that cannot change significantly from one nematic specimen to another.

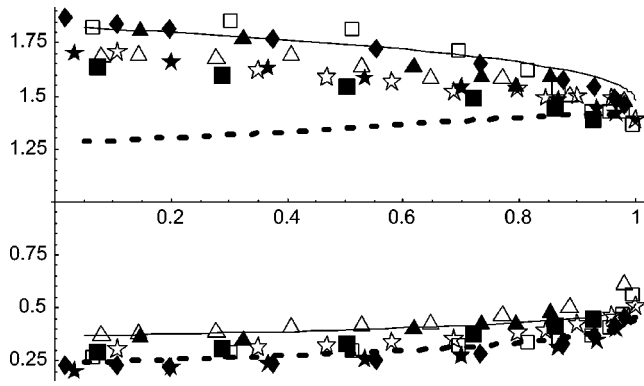


FIG. 2. In this figure results from different sources were used to furnish the ratios between the Miesowicz coefficients, η_3/η_2 and η_3/η_1 . In all data η_3/η_2 appears in the upper half of the picture, showing a regularity that suggests a universality. The data for η_3/η_1 appear in the lower half of the picture and also suggest a universality. The set of isolated points (the stars, triangles, squares, etc.) give the experimental result for these data, collected in the liquid crystal literature (the references are quoted in the text). The dotted lines give the predictions of the kinetic theory for these ratios. The continuous line gives the adjustment for the experimental data given by the model developed in this work. Observe that even predicting a universality, the results of the kinetic theory are in evident disagreement with the experimental data.

Consequently, these ratios must be approximately the same for all the nematic specimens for which the geometric proportions are equivalent and, hence, they express a universality of the nematic state. In order to study these results the values of S_2 and S_4 , calculated from the Maier-Saupe model [21,16], have been used. For the parameter p it has been used $p=10$. The results of these calculations are shown in Fig. 2 in the form of dotted lines.

III. EXPERIMENTAL RESULTS

In order to compare the above findings with experimental results, LC viscosity data points have been collected in the LC literature. The list of the compounds utilized in this analysis is given by PAA (p' -azoxyanisole), MBBA (p' -methoxybenzylidene- p - n -butylaniline), N4 (eutectic mixture of the 4-methoxy-4'- n -butylazoxybenzenes), EM (eutectic mixture of 4'- n -pentylphenyl 4-methoxybenzoate and 4'- n -pentylphenyl 4- n -hexyloxybenzoate), 5CBP (4- n -pentyl-4'-cyanobiphenyl), HBAB (p - n -hexyloxybenzylidene- p' -aminobenzonitrile), MIST (1:1:1-molar mixture of HBAB with p - n -butoxybenzylidene- p' -aminobenzonitrile and p - n -octanoyloxybenzylidene- p' -aminobenzonitrile) [22–29]. For all of these data the temperature was rescaled to a new and unique temperature scale; the two fixed points of this temperature scale have been chosen as the crystalline-nematic phase-transition point, for which was attributed the temperature $t=0$, and the nematic-isotropic phase-transition point, for which was attributed the temperature $t=1$. Afterwards, the ratios η_3/η_1 and η_3/η_2 have been computed for each compound of this set and the results collected in a unique graphic, as shown in Fig. 2. From this figure, we see

that the sets of points corresponding to n_3/n_1 and n_3/n_2 are not randomly distributed. The values of η_3/η_1 fluctuate around $\eta_3/\eta_1 \sim 0.4$, a small increase with the rising of the temperature being observed. The values of η_3/η_2 fluctuate around $\eta_3/\eta_2 \sim 1.7$, presenting a small decreasing with the rising of the temperature. Furthermore, both sets of experimental data points seem to approach 1 as the temperature approaches the N-I transition. Even presenting significant fluctuations, it is clear that these experimental data points occupy two distinct regions. The regularity and agreement observed on their distribution seem to be in accord with the idea of the existence of a physical rule connecting them; after a simple rescaling in the temperature, experimental data of different compounds, measured at different epochs by different researches, are clearly distributed along two distinct regions, suggesting that they could coalesce along two single curves, expressing a universal relationship.

Figure 2 also presents a comparison between the experimental data and the kinetic prediction. Without a doubt, the distributions observed on these experimental data do not agree with that theoretical calculations. While the theoretical predictions for the ratio η_3/η_1 can roughly describe the experimental observations, for η_3/η_2 the experimental and theoretical curves are in irreconcilable disagreement. Indeed, for η_3/η_2 , they only agree around $t=1$ and, as the temperature is diminished, the two curves produce completely different results. These same calculations have been done using other known kinetic [9–14] formulas for the Miesowicz coefficients and we have not found in the LC literature a theoretical prediction for η_3/η_2 that could explain, even approximately, the experimental findings. To understand why this happens, consider Eq. (1) and observe that when the region of the crystalline-nematic phase transition is approached, one would have $S_2 \sim 1$ and $S_4 \sim 1$. So at this limit one has

$$\eta_2 = \frac{0.6}{2} n \left(1 - \frac{6.6}{(p^2 + 1)^2} \right), \quad (2)$$

$$\eta_3 = \frac{0.6}{2} n. \quad (3)$$

Hence, this equation predicts that η_2 and η_3 would become nearly equal for $p > 3$, leading to the result observed in Fig. 2, $\eta_3/\eta_2 \approx 1$. Nevertheless, as can be seen in that figure, the set of experimental data points does not confirm this prediction, suggesting that at the region of the crystalline-nematic transition $\eta_3/\eta_2 \approx 1.75$.

If we remember that $S_2 \sim 1$ and $S_4 \sim 1$ implies that the angular fluctuations of the long axis of the nematic domain are nearly frozen, we see that it is the difference between these geometrical configurations that becomes relevant at this region. Consequently, at the point of neighborhoods of the crystalline-nematic phase-transition the form of the nematic domain and its packing must have a critical role in the nematic viscosities. That is, around this region the distribution of nematic domains around a given point and the short ranged steric interaction, which are modeled by the calamitic

shape of the nematic domains, cannot be ignored. This result explains some essential differences between the procedure that will be used ahead and the one usually followed by the kinetic approach. Doi's theory, and its improvements, is composed of two constitutive equations [12]: one determining the orientational distribution function and other expressing the stress tensor in terms of such a distribution function. The equation for the orientational distribution function gives explicit emphasis to the angular Brownian motion through the use of equations derived from the Smoluchowski, or Fokker-Planck equations [10]. Of course, this procedure is appropriated when the thermal vibration dominates the scene, as happens in the neighborhoods of the nematic-isotropic phase transition. But, as has been shown in detail above, such a procedure does not describe the measurements made at lower temperatures. At the region of the crystalline-nematic transition another approach must be tried; this is the aim of the following section.

IV. A GEOMETRICAL COMPUTATION OF THE MIESOWICZ COEFFICIENTS

In this section the ratio between the Miesowicz coefficients will be computed by means of an approach that emphasizes the geometry of the nematic phase through the explicit use of the nematic radial distribution function and the local steric volumetric exclusion. As our aim is only to illustrate how, near the crystalline nematic phase-transition point, these variables become important to the understanding of the viscosity of these materials, we have realized a simple analysis that, surely, lacks the formal rigor that a further analysis must accomplish. Nevertheless, as an example of how the geometry of the packing properties of the nematic phase has a decisive rheological function as the crystalline phase is approached such in procedure is admissible. Ahead, the final remarks of this work, we will comment on some of these points that, we think, deserve further analysis.

The starting point of our calculation is the known microscopic expression for a stress tensor [30],

$$\sigma_{\alpha,z} = -\frac{1}{2V} \sum_{m,n} \langle F_{m,n,\alpha} h_{m,n,z} \rangle, \quad h_{m,n,z} = R_{m,z} - R_{n,z}, \quad (4)$$

where V is volume of the sample, $F_{m,n,\alpha}$ gives the component α of the force that the molecule m positioned at \vec{R}_m exerts on the molecule n positioned at \vec{R}_n , $h_{m,n,z}$ gives the projection on the \vec{e}_z axis of the distance between them, and $\langle f \rangle$ is the thermodynamic mean of the function f . Our procedure will follow two steps. First, to ensure that the geometry of the local distribution of the nematic domains is being considered, the statistical averages will be taken with the use of the radial distribution function [31,32]. Second, to simulate the calamitic shape of the nematic domains, and its change with the temperature, a generalized coordinate system, the prolate spheroidal coordinate [33], will be used. Of course, if computed exactly, the procedure used in this paper and the one that uses the kinetic approach must lead to the

same results. The differences would appear when approximations are made; each one will stress different aspects of the same problem.

So, let $Z_2(\vec{r}_1, \vec{r}_2)$ be the usual [34] two-particle distribution function, which is used to compute statistical averages of a two-point function $f(\vec{r}_1, \vec{r}_2)$,

$$\langle f(\vec{r}_1, \vec{r}_2) \rangle = \int_V \int_V Z_2(\vec{r}_1, \vec{r}_2) f(\vec{r}_1, \vec{r}_2) d\vec{r}_1 d\vec{r}_2. \quad (5)$$

Then, making $\vec{r} = \vec{r}_1 - \vec{r}_2$, the relation

$$Z_2(\vec{r}_1, \vec{r}_2) d\vec{r}_1 d\vec{r}_2 = \rho^2 g(\vec{r}) d\vec{r} dV \quad (6)$$

defines the pair distribution function $g(\vec{r})$ of the system [34], where $\rho = N/V$ and N is the number of particles on the system. Consequently Eq. (4) can be written as

$$\sigma_{\alpha,z}^g = -\frac{\rho^2}{2} \int_V F_\alpha(\vec{r}) h_z^g(\vec{r}) g(\vec{r}) d\vec{r}, \quad (7)$$

where $F_\alpha(\vec{r})$ is the α component of the force between two particles, one located at the origin and the other located at r , and $h_z^g(\vec{r})$ gives the \vec{e}_z component of the distance between them. The superscript g has been introduced to reinforce that the distance between two particles along the \vec{e}_z direction surely depends on the orientation of the molecules and, consequently, on the distribution function g . This expression will be used to compute the translational viscosity of the system, consequently, to be in accord with the geometry established in Fig. 1; the direction between the molecular long axis, and the direction of the fluid flow will be changed to be in accord with the geometry required by the corresponding Miesowicz coefficient. Moreover, supposing that the force between the particles can be derived from a central potential $U(\vec{r})$, i.e., $F_\alpha(\vec{r}) = \partial_\alpha U(\vec{r})$,

$$\sigma_{\alpha,z}^g = -\frac{\rho^2}{2} \int_V h_z^g(\vec{r}) g(\vec{r}) \partial_\alpha U(\vec{r}) d\vec{r}. \quad (8)$$

An immediate result of this equation is that if the radial distribution $g(\vec{r})$ is symmetric by reflection in a plane perpendicular to the \vec{e}_z axis, then the stress tensor will become null because $h_z^g(\vec{r})$ will change sign by such reflection [the central potential $U(\vec{r})$ is always symmetric with respect to such reflection]. Consequently, considering that when the fluid is at rest $g(r)$ is necessarily symmetric by reflection with respect to any plane, the only way to avoid this null result is to admit that the existence of a gradient in the velocity of the fluid along the \vec{e}_z direction breaks this symmetry. That is, the presence of a shearing flow must change the radial distribution function $g \rightarrow g + \Delta g$ leading to a non-null result in Eq. (8). So, Δg must be a function of $\partial_z V_x$, i.e.; $\Delta g = \Delta g(\partial_z V_x)$, satisfying the condition $\lim_{\partial_z V_x \rightarrow 0} \Delta g = 0$. As a result, in first order on shearing flow, one has $\Delta g \sim \alpha \partial_z V_x$. To find an explicit form to α the relaxation time

approach can be used [18]. So, consider that shearing flow happens along the \vec{e}_x direction and that during a time interval Δt a fluid element undergoes the displacement $\Delta x = x(t + \Delta t) - x(t) = V_x \Delta t$. Further, assume the existence of a relaxation time τ , and that $\Delta t \approx \tau$. With these hypotheses the corresponding change in g will be given by

$$\Delta g = \frac{dg}{dx} \frac{dx}{dt} \Delta t, \quad (9)$$

$$\approx \tau \frac{dg}{dx} z \partial_z V_x, \quad (10)$$

where it has been assumed that $\partial_z V_x$ is a constant and, consequently, $V_x = z \partial_z V_x$. So, $\alpha = \tau z dg/dx$ and the non-null term of Eq. (8) becomes

$$\sigma_{x,z}^g = -\tau \frac{\rho^2}{2} \partial_z V_x \int_V z h_z^g(\vec{r}) \partial_x g \partial_x U d\vec{r}. \quad (11)$$

To compute the viscosity η we remember that by definition $\eta = \sigma_{x,z} / \partial_z V_x$, which gives

$$\eta^g = -\tau \frac{\rho^2}{2} \int_V z h_z^g(\vec{r}) \partial_x g \partial_x U d\vec{r}. \quad (12)$$

In order to compute the above integral a special coordinate system will be used, the prolate spheroidal coordinates [33], Fig. 3, which is described by

$$\begin{aligned} x_1 &= d \sinh(\mu) \sin(v) \cos(\varphi), \\ x_2 &= d \sinh(\mu) \sin(v) \sin(\varphi), \\ x_3 &= d \cosh(\mu) \cos(v), \end{aligned} \quad (13)$$

where $x_1, x_2,$ and x_3 define a Cartesian coordinate system fixed on the molecule and μ, v, φ are generalized coordinates describing a radial variable μ , and two angular variables, v and φ , d being the focal distance. The choice of such a coordinate system is motivated by the fact that it gives a good simulation of the nematic domain. Assuming a shearing flow along the \vec{e}_x axis, as shown in Fig. 1, the three different ways by which the molecular axis (x_1, x_2, x_3) may become coincident with the laboratory coordinates (x, y, z) will give us the geometry of the three distinct Miesowicz coefficients. So, as can be seen in Fig. 1, when $x_1 \rightarrow x, x_2 \rightarrow y,$ and $x_3 \rightarrow z$, we have the geometry of the Miesowicz coefficients, η_1 . Performing a clockwise rotation of $\pi/2$ of this configuration around the x_2 axis, that is, $x_1 \rightarrow -z, x_2 \rightarrow y$ and $x_3 \rightarrow x$, the geometry of the second Miesowicz coefficient η_2 is produced. Finally, with further clockwise rotation of $\pi/2$ around x_1 , where $x_1 \rightarrow -z, x_2 \rightarrow z,$ and $x_3 \rightarrow y$ will produce the geometry of the third Miesowicz coefficient η_3 .

To proceed, it is made the further supposition that the interaction between the particles depends only on the radial coordinate μ , being independent of the angular variables v and φ . That is, $U = U(\mu)$. As a consequence the radial dis-

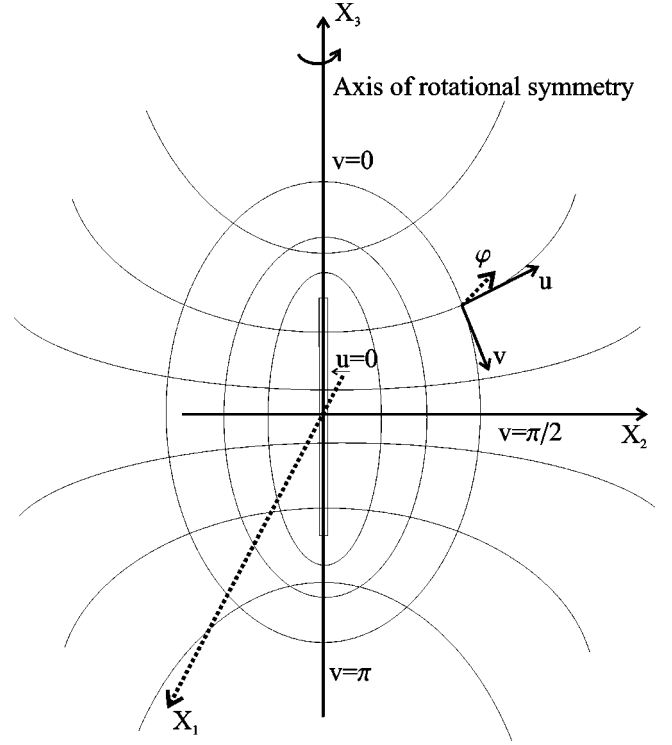


FIG. 3. Geometry of the prolate spheroidal coordinate. The axes $x_1, x_2,$ and x_3 are fixed on the molecule and as they rotate in relation to the axes $x, y,$ and z , fixed on the laboratory, as a new physical condition is produced, and a different viscosity is produced.

tribution function would also be limited to depending only on $\mu, g \equiv g(\mu)$. To write Eq. (1) in terms of this coordinate system the rules of transformation for each term of this equation must be known. Here, this will be done explicitly for η_1 ; analogous expressions can be found for η_2 and η_3 . Of course, $\partial_x U \rightarrow \partial_x \mu \partial_\mu U$ and $\partial_x g \rightarrow \partial_x \mu \partial_\mu g$. Then

$$\begin{aligned} \eta_1 &= -\tau \frac{\rho^2}{2} \int_V z_1(\mu, v, \varphi) h_{1z}(\mu, v, \varphi) \\ &\quad \times \left(\frac{\partial \mu}{\partial x} \right)^2 \partial_\mu g \partial_\mu U J d\mu dv d\varphi, \end{aligned} \quad (14)$$

where J is the Jacobian of the transformation. For the geometrical configuration of η_1 , we have

$$z(\mu, v, \varphi) = d \cosh \mu \cos v,$$

$$h_z^1(\mu, v, \varphi) = 2d \cosh \mu,$$

$$\frac{\partial \mu}{\partial x} = -\frac{2 \cos \varphi \cosh \mu \sin v}{d(\cos 2v - \cosh 2\mu)},$$

$$J = d^3 \sin v \sinh \mu (\sin^2 v + \sinh^2 \mu),$$

giving

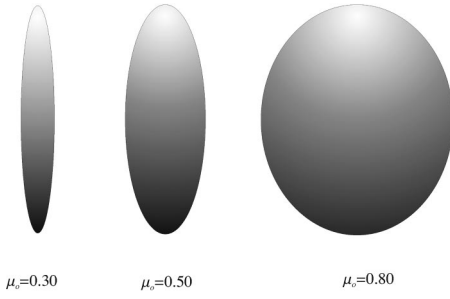


FIG. 4. Variation of the shape of an ellipsoid of revolution, given by the prolate spheroidal coordinate, when the parameter μ_o is changed. This figure represents the change of the effective form of a nematic domain with the temperature.

$$\eta_1 = -2d^3 \rho^2 \tau \int_V \frac{\cosh^4 \mu \sinh \mu \cos v \sin^3 v \cos^2 \varphi}{\cos 2v - \cosh 2\mu} \times \partial_{\mu} g \partial_{\mu} U d\mu dv d\varphi. \quad (15)$$

As $\partial_{\mu} g$ and $\partial_{\mu} U$ depend only on μ the integration on v and φ can be done, giving

$$\eta_1 = -2\pi d^3 \rho^2 \tau \int \cosh^4 \mu \sinh \mu \times [1 + \log(\tanh^2 \mu) \sinh^2 \mu] \partial_{\mu} g \partial_{\mu} U d\mu. \quad (16)$$

To proceed we remember that

$$\partial_{\mu} U = -[\partial_{\mu}(\exp(-\beta U))] \exp(\beta U) / \beta,$$

and take advantage of the presence of the hard core of U around the position μ_o to write $\partial_{\mu}(\exp(-\beta U)) \approx \delta(\mu - \mu_o)$ (about the physical meaning of this approximation see, for example, Ref. [31]). Consequently we have

$$\frac{\eta_3}{\eta_1} = \frac{2 \sec h \mu_o (\cosh \mu_o + 2 \sinh 2\mu_o) (\cosh 2\mu_o - \sinh 2\mu_o) \tanh^2 \mu_o}{3(1 + \log(\tanh^2 \mu_o) \sinh^2 \mu_o)}, \quad (21)$$

$$\frac{\eta_3}{\eta_2} = \frac{1}{3} \coth \mu_o (1 + \coth \mu_o), \quad (22)$$

and through the parameter μ_o , these ratios between the Miesowicz coefficients are dominated by the geometrical character of the nematic domains. To see the physical importance of the geometry on these ratios let us consider Fig. 4, where nematic domains with $\mu_o = 0.30, 0.50, 0.80$ are shown. As can be observed in these figures as μ_o increases the nematic domains become more and more spherical, losing the nematic order. Thus μ_o can be used to represent the effective shape of the nematic domains affording the supposition that it is a function of the order parameter $\mu_o = \mu_o(S)$. Furthermore, according to this figure it is expected

$$\eta_1 = 2G \cosh^4 \mu_o \sinh \mu_o [1 + \log(\tanh^2 \mu_o) \sinh^2 \mu_o], \quad (17)$$

where

$$G = \frac{\pi d^3 \rho^2 \tau}{\beta} \exp[\beta U(\mu_o)] \partial_{\mu} g /_{\mu = \mu_o}. \quad (18)$$

Using the same procedure, analogous expressions can be found for η_2 and η_3 ,

$$\eta_2 = 2G \sinh^4 \mu_o \cosh \mu_o (\cosh 2\mu_o - \sinh 2\mu_o), \quad (19)$$

$$\eta_3 = \frac{G}{3} \sinh^3 \mu_o (\cosh 2\mu_o - \sinh 2\mu_o) \times (1 + \cosh 2\mu_o + 2 \sinh 2\mu_o). \quad (20)$$

V. UNIVERSALITY

The general form of the viscosity coefficients found in the preceding section is, in at least one aspect, very similar to those found in the kinetic theory. In both cases these expressions can be separated into two parts; one, G , which is the same for all Miesowicz's coefficients, express the thermodynamical properties that can be used to identify a specific nematic material, and the other, which is essentially geometric, distinguishes one viscosity coefficient from another. Consequently, as happened in the kinetic theory, the ratios between these expressions cancel the common term that identify a particular material and all that remains is a set of equations expressing some general and universal properties of the nematic material. Thus, as long as the above approximations are valid, we have

that μ_o increases when S diminishes and, due to the phase transition for small S , it could be supposed that

$$\mu_o = \frac{a}{S^b}, \quad (23)$$

where a and b are constants. Considering also that the order parameter can be expressed in terms of the rationalized temperature [20,21], $S \sim \sqrt{1-t}$ where $t = T/T_c$ and T_c is the temperature of nematic-isotropic phase transition point, Eq. (23) can be also expressed as

$$\mu_o = \frac{\alpha}{(1-t)^\gamma}, \quad (24)$$

where the coefficients α and γ have to be found experimentally.

Even being possible to find the values of α and γ through adjusts with experimental results an argument suggesting a value for γ will present here. The balance between the interactions taking place at the nematic domains and its thermal vibrations leads to the variations of the molecular shape, shown in Fig. 4, provoking the changes in the order parameter observed in the experiments. Considering that the molecular interactions are well described by the Lennard-Jones potential

$$U(\mu_o) = \epsilon \left[\left(\frac{\sigma}{\mu_o} \right)^{12} - \left(\frac{\sigma}{\mu_o} \right)^6 \right], \quad (25)$$

where ϵ and σ are constants, and that the thermal vibrations are proportional to the temperature, $E_t = N/2K_B T$, where N is the number of moles and K_B is the Boltzmann constant, it can be said that the energy of a nematic domain is approximately given by

$$E = \frac{N}{2} K_B T + \epsilon \left[\left(\frac{\sigma}{\mu_o} \right)^{12} - \left(\frac{\sigma}{\mu_o} \right)^6 \right]. \quad (26)$$

This predicts that for a stable condition the range of the nematic domain μ_r would be given by

$$\mu_o = \sigma \left(\frac{\sqrt{\epsilon}(\sqrt{\epsilon} + \sqrt{4E + 2NK_B T - \epsilon})}{NK_B T - 2E} \right)^{1/6}. \quad (27)$$

According to these last two equations when $T \rightarrow T_c = 2E/NK_B$ the thermal energy would dominate the energy of the nematic configuration leading to a divergence of μ_o with the form $\mu_o \sim (T - T_c)^{1/6}$.

Of course, all the reasoning leading to this result is a roughly approximation of a very complex situation. But there is an essential result on it, when it is compared with Eq. (24) one sees that $\gamma = 1/6$, and that equation becomes

$$\mu = \frac{\alpha}{S^{1/3}}. \quad (28)$$

The important consequence of this relation is that it predicts that all experimental results would be described with the adjust of a unique experimental parameter, α . The continuous lines of Fig. 2 give the best fit obtained with $\alpha = 0.68$.

VI. FINAL REMARKS AND CONCLUSION

Along this work we have shown that geometrical form in which the nematic domains are aggregated to form the liquid crystal cannot be ignored when the rheological properties of such materials are computed and the effects of such omission are particularly important at the neighborhoods of the crystalline-nematic phase-transition point. Furthermore, with these geometrical properties the universal behavior observed in the ratio between the Miesowicz coefficients could be explained. In order to establish this universal law we have used the results of the kinetic theory, some experimental data

available in the LC literature and computed these ratios through an independent way. All these approaches predict the existence of such universal relation. However, when compared with known experimental data, one of the curves predicted by the kinetic theory does not agree with the general trends observed in the distribution of the data points. Indeed, only in the neighborhoods of the nematic-isotropic phase transition, does the kinetic theory have some concordance with the experiment, and as the crystalline-nematic transition point is approached, these two curves present an irreconcilable disagreement. The reason for this is that, according to the calculations of the kinetic theory, when the order parameters S_2 and S_4 approach the crystalline phase the two Miesowicz coefficients η_2 and η_3 , would become essentially equal. However, these two configurations are clearly so different that it is impossible to believe that the prediction of equal viscosities could make any physical sense; indeed the experimental results corroborate this doubt showing that the measured viscosities are actually completely different. In order to overcome these difficulties it has been supposed that the observed deviation of the kinetic theory from the experimental data comes from the fact that some aspects of the geometry of the nematic structure, which are essential in the neighborhoods of the crystalline-nematic transition, have not been taken into account. So, in order to consider these aspects, the radial distribution functions have been used in the statistical averages and, furthermore, through the use of an appropriated coordinate system, the geometry of the nematic domains and the steric interaction between them have been considered. Finally, our results also have predicted a universal law for the ratio between the Miesowicz coefficients that describes efficiently the experimental data.

Nevertheless, as have been pointed out before, there are some aspects of our calculations that deserve further comments. Let us begin by adverting that Eq. (9) assumes that the radial distribution function describing a fluid flow can be obtained by continuous extension of that describing a stationary solution. As has been noticed in the text such an approach is equivalent to the relaxation time approximation (see, for example, Eq. (13.5.6) of Ref. [18]) and, of course, an improved kinetic approach, in which stationary solutions arise naturally, would be required. In the same way, Eqs. (23), (24), assume that an effective shape of the nematic domain, as shown in the Fig. 4, is a function of the order parameter and, consequently, of the corresponding reduced temperature. Clearly, this is an *ad hoc* hypothesis that was made with the unique purpose of giving emphasis to the geometry of the nematic cell. Likewise, the thermal arguments leading to the power 1/3 to S , at Eq. (28), were introduced to avoid considering it as a parameter to be adjusted with the use of the experimental points. That is, that reasoning has the aim of showing that very simple arguments can be used to evaluate the term relating the shape of the nematic domain with the temperature. Synthesizing, along the approach that leads to the continuous curve shown in Fig. 2 some *ad hoc* hypotheses, which must be further investigated, were made. Nevertheless, all of them have had the objective of revealing the importance of the geometry of the nematic packing to the understanding of the universalities that have

been found in the viscosities of the liquid crystals.

Finally, let us observe that in the last few years a set of results has been published in which the viscosity of the nematic materials has been calculated using some interesting geometrical arguments in which through an affine transformation the viscosities of a perfect aligned nematic fluid composed by ellipsoidal domains are mapped on the viscosity of a fluid of spherical domains [35,36]. Afterwards, a prescription of how to associate this perfect aligned nematic fluid with the viscosity of a real fluid was suggested. Due to the nature of such approach, some interesting questions can be formulated about the interconnection between these results and the ones that achieved along this paper. For example, is

it capable to describe correctly the universality that we have described above? Does it give correct descriptions of the nematic viscosities at the neighborhoods of the nematic-crystalline transition? As such approach is essentially geometric, it is hoped that it could help us in the research suggested by this paper and form the subject of a further study.

ACKNOWLEDGMENTS

The financial support of the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) and Fundação Araucária is acknowledged.

-
- [1] M. Miesowicz, *Nature (London)* **136**, 261 (1935).
 [2] M. Miesowicz, *Bull. Int. Acad. Polon. Sci. Lett. Ser. A* **1936**, 228 (1936).
 [3] J.L. Ericksen, *Arch. Ration. Mech. Anal.* **4**, 231 (1960); **9**, 371 (1962).
 [4] F.M. Leslie, *Q. J. Mech. Appl. Math.* **19**, 357 (1966).
 [5] O. Parodi, *J. Phys. (Paris)* **31**, 581 (1970).
 [6] D. Foster, T. Lubensky, and P. Pershan, *Phys. Rev. Lett.* **26A**, 1016 (1971).
 [7] P.C. Martin, O. Parodi, and P. Pershan, *Phys. Rev. A* **6**, 2401 (1972).
 [8] P.C. Martin, P.J. Pershan, and J. Swift, *Phys. Rev. Lett.* **25**, 844 (1970).
 [9] M. Doi and S. F. Edwards, *The Theory of Polymer Dynamics* (Oxford Press, New York, 1986).
 [10] M.A. Osipov and E.M. Terentjev, *Z. Naturforsch., A: Phys. Sci.* **44**, 785 (1989); *Mol. Cryst. Liq. Cryst.* **198**, 428 (1990); *Riv. Nuovo Cimento* **12**, 1223 (1990).
 [11] M. Doi and F. Edwards, *J. Chem. Soc., Faraday Trans. 1* **74**, 560 (1978); *F. Edward*, **74**, 918 (1978).
 [12] N. Kuzuu and M. Doi, *J. Phys. Soc. Jpn.* **52**, 3486 (1983); **53**, 1031 (1984).
 [13] G. Marrucci, *Mol. Cryst. Liq. Cryst. Lett.* **72**, 153 (1982).
 [14] T.R. Kikpatric, *J. Chem. Phys.* **89**, 5020 (1988).
 [15] M. Simões and S.M. Domiciano, *Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A* **367**, 1 (2001).
 [16] R.G. Larson and L.A. Archer, *Liq. Cryst.* **19**, 883 (1995).
 [17] R.G. Larson, *The Structure and Rheology of Complex Fluids* (Oxford University Press, Oxford, 1999).
 [18] R. Reif, *Fundamentals of Statistical and Thermal Physics* (McGraw-Hill, Kogakusha, Ltd., Tokyo, Japan 1965).
 [19] K. Huang, *Statistical Mechanics* (Wiley, New York, 1963).
 [20] P.G. de Gennes and J. Prost, *The Physics of Liquid Crystals*, 2nd ed. (Clarendon Press, Oxford, 1993).
 [21] W. Maier and A. Saupe, *Z. Naturforsch. A* **13A**, 564 (1958); **14A**, 882 (1959); **15A**, 287 (1960).
 [22] H. Tseng and B. A. Finlayson, *Mol. Cryst. Liq. Cryst.* **116**, 265 (1985).
 [23] H. Kneppel, F. Scheneider, and N.K. Sharma, *Ber. Bunsenges. Phys. Chem.* **85**, 784 (1981).
 [24] C.H. Gahwiller, *Mol. Cryst. Liq. Cryst.* **20**, 301 (1972).
 [25] W.H. de Jeu, W.A.P. Claassen, and A.M.J. Spruijt, *Mol. Cryst. Liq. Cryst.* **37**, 269 (1976).
 [26] M.G. Kim, S. Park, Sr. M. Cooper, and S.V. Letcher, *Mol. Cryst. Liq. Cryst.* **36**, 143 (1976).
 [27] N.V. Madhusudana, P.P. Karat, and S. Shandrasekhar, *Pramana, Suppl.* **1**, 225 (1975).
 [28] G.P. Chen, H. Takezoe, and A. Fukuda, *Liq. Cryst.* **5**, 347 (1989).
 [29] Chmielewski, *Mol. Cryst. Liq. Cryst.* **132**, 339 (1986).
 [30] See Eq. (3.130) of the Ref. [9] above.
 [31] J.A. Barker and D. Henderson, *Rev. Mod. Phys.* **48**, 587 (1976).
 [32] C.A. Croxton, *Introduction to Liquid State Physics* (Wiley, New York, 1975).
 [33] G. Arfken, *Mathematical Methods for Physicists* (Academic Press, New York, 1966).
 [34] R.K. Pathria, *Statistical Mechanics* (Pergamon Press, New York, 1972).
 [35] D. Baalss and S. Hess, *Z. Naturforsch. Teil A* **43**, 662 (1988).
 [36] H. Ehrentraut and S. Hess, *Phys. Rev. E* **51**, 2203 (1995).