

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/238038842>

# A reply to Shahinpoor's comments on 'Alignment of nematic liquid crystals'

ARTICLE *in* THE JOURNAL OF CHEMICAL PHYSICS · JANUARY 1975

Impact Factor: 2.95 · DOI: 10.1063/1.431432

---

CITATIONS

2

---

READS

5

2 AUTHORS, INCLUDING:



[James D. Lee](#)

George Washington University

**148** PUBLICATIONS **1,874** CITATIONS

SEE PROFILE

## A reply to Shahinpoor's comments on "Alignment of nematic liquid crystals"

James D. Lee and A. Cemal Eringen

Citation: *J. Chem. Phys.* **63**, 1321 (1975); doi: 10.1063/1.431432

View online: <http://dx.doi.org/10.1063/1.431432>

View Table of Contents: <http://jcp.aip.org/resource/1/JCPSA6/v63/i3>

Published by the AIP Publishing LLC.

---

### Additional information on J. Chem. Phys.

Journal Homepage: <http://jcp.aip.org/>

Journal Information: [http://jcp.aip.org/about/about\\_the\\_journal](http://jcp.aip.org/about/about_the_journal)

Top downloads: [http://jcp.aip.org/features/most\\_downloaded](http://jcp.aip.org/features/most_downloaded)

Information for Authors: <http://jcp.aip.org/authors>



**Goodfellow**

metals • ceramics • polymers  
composites • compounds • glasses

**Save 5% • Buy online**

**70,000 products • Fast shipping**

[www.goodfellowusa.com](http://www.goodfellowusa.com)

# A reply to Shahinpoor's comments on "Alignment of nematic liquid crystals"

James D. Lee and A. Cerná Eringen

George Washington University, Washington, D.C. 20006  
and Princeton University, Princeton, New Jersey 08540  
(Received 16 September 1974)

Shahinpoor, in his comments, claimed the following.

(i) The equations we employed to analyze steady state viscosity of nematic liquid crystals are those of Leslie, not ours, since our constitutive equations will not reduce to those of Leslie, in this special case.

(ii) If our "mathematically derived" constitutive equations are employed, then the steady state shear flow of nematic liquid crystals is not possible.

We cannot agree with Shahinpoor's comments. The problem of Shahinpoor stems from the fact that he did not read our papers carefully, and hence did not catch the concept of the *reference state* which we tried to convey through our papers (his Refs. 1, 2) and the multitude of applications contained therein.

As against Shahinpoor's claim, first we shall show that our constitutive equations for nematic liquid crystals

$$t_{ij} = -p\delta_{ij} + A_{KLMN}\hat{C}_{MN}x_{i,K}x_{j,L}, \quad (1)$$

$$m_{ij} = \left[ \left( \frac{\rho}{\rho_0} \right) B_{LKMN}\Gamma_{MN} + b_{LKMN}\dot{\Gamma}_{MN} \right] x_{i,K}x_{j,L}$$

under the reference state hypothesis go into

$$t_{ij} = -p\delta_{ij} + a_{ijmn}(v_{n,m} - \epsilon_{mnp}v_p), \quad m_{ij} = b_{ijmn}v_{mn} \quad (2)$$

$$a_{ijmn} \equiv A_{KLMN}\delta_{iK}\delta_{jL}\delta_{mM}\delta_{nN}, \quad b_{ijmn} \equiv B_{LKMN}\delta_{iK}\delta_{jL}\delta_{mM}\delta_{nN} \quad (3)$$

which are used in our analysis of shear flow. Here  $\delta_{iK}$  are the direction cosines between the coordinates of the reference state and that of the spatial coordinates. Note the important fact that  $A_{KLMN}$  and  $B_{LKMN}$  are material moduli but not  $a_{ijmn}$  and  $b_{ijmn}$ , and, of course,  $\delta_{iK}$  are not necessarily Kronecker deltas.

The reference state hypothesis stipulates that: "Any state in which  $\rho = \rho_0$  and  $\chi_{hK,L} = 0$  is a reference state."

Now first we note that his Eq. (1.6)<sub>2</sub> of his comments is wrong. This is because at a reference state  $\chi_{hK,L}$  vanishes, but  $\dot{\chi}_{hK,L}$  need not vanish, in fact

$$\dot{\chi}_{hK,L} = \frac{D}{Dt}(\chi_{hK,L}) = -(\epsilon_{hlm}v_m\chi_{lK}),_L = -\epsilon_{hlm}v_{m,n}x_{n,L}\chi_{lK} \quad (4)$$

since  $\dot{\chi}_{hK} = \epsilon_{hlm}v_m\chi_{lK}$ . Clearly  $\chi_{iK,L} = 0$ , but since  $v_{m,n} \neq 0$ , in general, his conclusion (1.6)<sub>2</sub>, namely,  $m_{ij} = 0$  is incorrect.

Next we show that under the reference state hypothesis (1) goes into (2). We shall do the analysis in a simple way so that it could be understood by everyone who can differentiate. At the same time, this approach will provide a systematic method to place the application of the reference state hypothesis to a "higher plane of generality" as desired by a referee during the period of com-

munication.

A nematic liquid crystal during its motion and deformation, in general, acquires many *reference states*. The state of the body at time  $t$  must be calculated with respect to the reference state that is nearest to the state at time  $t$ , since all past histories prior to the nearest reference state are wiped out. Let  $X_{K_0}$  and  $\Xi_{K_0}$  denote, respectively, the fixed rectangular coordinates of a point  $P$  and the director at  $P$  in the body  $V_0$ , at an initial time  $t = 0$ . The motion and the director at any other time  $t$  are described by

$$x_k = x_k(\mathbf{X}_0, t) \rightarrow X_{K_0} = X_{K_0}(\mathbf{x}, t),$$

$$\xi_k = \chi_{hK_0}(\mathbf{X}_0, t) \Xi_{K_0} \rightarrow \Xi_{K_0} = \chi_{hK_0}(\mathbf{x}, t) \xi_h. \quad (5)$$

If at time  $\tau$ ,  $0 \leq \tau \leq t$ , the body acquires a reference state. Then we have  $\det[x_{h,K_0}(\mathbf{X}_0, \tau)] = 1$ ,  $\chi_{hK_0,L_0}(\mathbf{X}_0, \tau) = 0$  for all  $X_{K_0} \in V_0$ . The position vector and the director at the reference state, at time  $\tau$ , are given by  $\hat{x}_k = x_k(\mathbf{X}_0, \tau)$ ,  $\hat{\xi}_k = \chi_{hK_0}(\mathbf{X}_0, \tau) \Xi_{K_0}$ . We erect a coordinate system  $X_K$  at this reference state (at time  $\tau$ ) in such a way that  $\hat{x}_k = \delta_{hK}X_K$ ,  $\hat{\xi}_k = \delta_{hK}\Xi_K$ . We may choose the  $X_3$  axis, of the  $X_K$  coordinate system, to be parallel to the axis of orientation at time  $\tau$ , namely, let  $\delta_{hK}$  be identical to  $\chi_{hK_0}(\mathbf{X}_0, \tau)$ , in order to simplify the material symmetry restrictions. It should be kept in mind that, in general, not every state is a reference state and not every axis is an axis of orientation. Now the deformation gradients  $x_{h,K}(t, \tau)$  and the microrotation  $\chi_{hK}(t, \tau)$ , at time  $t$  referred to the reference state at time  $\tau$ , are calculated by

$$x_{h,K}(t, \tau) = \frac{\partial x_h}{\partial \hat{x}_i}(\mathbf{X}_0, t) \delta_{iK} = x_{h,K_0}(\mathbf{X}_0, t) X_{K_0,I}(\hat{\mathbf{x}}, \tau) \delta_{iK} \quad (6)$$

$$\chi_{hK}(t, \tau) = \frac{\partial \xi_h}{\partial \hat{\xi}_i}(\mathbf{X}_0, t) \delta_{iK} = \chi_{hK_0}(\mathbf{X}_0, t) \chi_{iK_0}(\mathbf{X}_0, \tau) \delta_{iK}.$$

Consequently

$$\chi_{hK_0,L}(t, \tau) = \frac{\partial \chi_{hK}(t, \tau)}{\partial \hat{x}_i} \delta_{iL}$$

$$= \chi_{hK_0,L_0}(\mathbf{X}_0, t) X_{L_0,I}(\hat{\mathbf{x}}, \tau) \chi_{mK_0}(\mathbf{X}_0, \tau) \delta_{iL} \delta_{mK}. \quad (7)$$

The Cosserat strain measures  $\mathbb{C}_{KL}(t, \tau)$  and  $\Gamma_{KL}(t, \tau)$ , at time  $t$  with respect to the reference state at time  $\tau$ , are defined, as usual, by

$$\mathbb{C}_{KL}(t, \tau) \equiv x_{h,K}(t, \tau) \chi_{hL}(t, \tau),$$

$$\Gamma_{KL}(t, \tau) \equiv \frac{1}{2} \epsilon_{KMN} \chi_{hM,L}(t, \tau) \chi_{hN}(t, \tau). \quad (8)$$

The material derivatives of these are

$$\begin{aligned}\hat{\mathcal{G}}_{KL}(t, \tau) &= (v_{i,k} - \epsilon_{klp} v_p) x_{k,K_0} X_{K_0,p}(\tau) \chi_{iL_0} \chi_{nL_0}(\tau) \delta_{mK} \delta_{nL} \\ \hat{\Gamma}_{KL}(t, \tau) &= \frac{1}{2} \epsilon_{KMN} \epsilon_{kmn} v_k x_{i,K_0} X_{L_0,p}(\tau) \chi_{mM_0} \chi_{nM_0}(\tau) \\ &\quad \times \chi_{nN_0} \chi_{sN_0}(\tau) \delta_{sN} \delta_{qM} \delta_{pL},\end{aligned}\quad (9)$$

where  $X_{K_0,k}(\tau) \equiv X_{K_0,k}(\mathbf{x}, \tau)$ ,  $\chi_{kK_0}(\tau) \equiv \chi_{kK_0}(\mathbf{X}, \tau)$ . Then the stress and moment stress at time  $t$  with respect to the reference state at time  $\tau$  are given by

$$\begin{aligned}t_{ij}(t, \tau) &= -p\delta_{ij} + A_{KL MN} \hat{\mathcal{G}}_{MN}(t, \tau) x_{i,K}(t, \tau) \chi_{jL}(t, \tau), \\ m_{ij}(t, \tau) &= [(\rho/\rho_0) B_{LK MN} \Gamma_{MN}(t, \tau) + b_{LK MN} \hat{\Gamma}_{MN}(t, \tau)] \\ &\quad \times x_{i,K}(t, \tau) \chi_{jL}(t, \tau).\end{aligned}\quad (10)$$

The anisotropy of the material moduli  $A$ ,  $B$ , and  $b$  is referred to the axis of orientation at time  $\tau$ . Since the state at time  $\tau$  is a reference state, by definition we have, at time  $\tau$ ,  $\rho = \rho_0$ ,  $\chi_{kK_0,L_0}(\mathbf{X}_0, \tau) = 0$ , and substitution of (9) into (10) gives precisely (2), which proves our assertion.

Thus the shear flow and other problems discussed in our work (his Refs. 1 and 2) are correct beyond any doubt. Note that in the case of rectilinear shear flow in the direction of orientation  $\delta_{kK}$  are Kronecker deltas since the motion does not change the direction of orienta-

tion and the state at any time  $t$  is a reference state.

Shahinpoor's difficulty stems from the fact that he pays no attention to the intermediate or nearest reference state and applies our equations to the reference state at time  $t=0$ , thus resulting in his erroneous Eq. (1.8). Using the leverage of this same error, he also tried to cast suspicion to our work on cholesteric liquid crystals.

Finally, while we do not intend to discuss priorities raised by his comment regarding Leslie's paper (his Ref. 3), we would like to point out that the *basis* of our theory was established several years prior to Leslie's work (cf. Refs. 1 to 5), and full comparison to our theory with that of the Ericksen-Leslie theory is made in Ref. 6.

<sup>1</sup>A. C. Eringen and E. S. Suhubi, *Int. J. Eng. Sci.* 2, 389 (1964).

<sup>2</sup>A. C. Eringen, *Int. J. Eng. Sci.* 2, 205 (1964).

<sup>3</sup>A. C. Eringen, *Proceedings of the Eleventh International Congress of Applied Mechanics* (Springer-Verlag, Berlin, 1966).

<sup>4</sup>A. C. Eringen, *J. Math. & Mech.* 16, 1 (1966).

<sup>5</sup>A. C. Eringen, *Int. J. Eng. Sci.* 5, 191 (1967).

<sup>6</sup>A. C. Eringen and J. D. Lee, *Liquid Crystals and Ordered Fluids*, edited by J. F. Johnson and R. S. Porter (Plenum, New York, 1974), Vol. 2.

## Photoelectron spectrum and structure of $\text{GaI}_3$

Klaus Wittel\*

*Institute of Inorganic Chemistry II, University of Frankfurt, BRD-6 Frankfurt, Germany*

Rolf Manne

*Department of Chemistry, University of Bergen, N-5014 Bergen, Norway*  
(Received 26 March 1975)

Dehmer *et al.* recently published the uv photoelectron spectra of gallium and indium trihalides.<sup>1</sup> Assuming planar ( $D_{3h}$ ) geometry they assigned the spectra using semiempirical molecular orbital calculations. The spectra of the bromides and iodides, like those of other heavy halides, show strong effects of spin-orbit interaction which were interpreted on a pseudoatomic basis. Because of the splitting of the  $1e''$  ionization energies (I  $5p\pi$  nonbonding orbitals) in  $\text{GaI}_3$  the conclusion was made that either the ground state or the corresponding  $E''$  states of the ion are pyramidal ( $C_{3v}$ ). The purpose of this comment is to show that the observed splitting is readily explained by higher-order spin-orbit interaction in planar  $D_{3h}$  geometry. The previous conclusion about a pyramidal geometry thus has to be reconsidered.

Spin-orbit interaction in the photoelectron spectra of  $\text{BBr}_3$  and  $\text{BI}_3$  was recently considered by the present authors<sup>2</sup> and the analysis for these molecules applies to  $\text{GaI}_3$  as well. For a qualitative argument we consider only the 9 iodine  $5p$  orbitals which may be selected as one set of  $\sigma$  orbitals, one set of "ordinary"  $\pi$  orbitals

perpendicular to the molecular plane, and one set of "in-plane" or  $\pi'$  nonbonding orbitals. In the simple  $D_{3h}$  group the  $\sigma$  orbitals transform according to the  $a'_1$  and  $e'$  representations, the  $\pi$  orbitals according to  $a'_2$  and  $e''$ , and the  $\pi'$  orbitals according to  $a'_2$  and  $e'$ .

In the  $D'_{3h}$  double group there are three irreducible representations corresponding to half-integer spin,  $e_{1/2}$ ,  $e_{3/2}$ , and  $e_{5/2}$ .<sup>3</sup> The spin functions  $\alpha$  and  $\beta$  transform according to  $e_{1/2}$ , and the transformation properties of the molecular spin orbitals follow from the direct products:  $a'_1 \times e_{1/2} = a'_2 \times e_{1/2} = e_{1/2}$ ;  $a'_2 \times e_{1/2} = e_{5/2}$ ;  $e' \times e_{1/2} = e_{3/2} + e_{5/2}$ ;  $e'' \times e_{1/2} = e_{1/2} + e_{3/2}$ . With the basis orbitals chosen there are no diagonal elements of the atomiclike spin-orbit interaction operators. Instead, the spin-orbit interaction connects those orbitals which belong to the same irreducible representation of the double group. In a Hückel scheme all off-diagonal elements have the same absolute magnitude, i.e.,  $1/2$  of the iodine spin-orbit parameter  $\zeta$ .<sup>2</sup> In addition, there are off-diagonal elements of the ordinary, nonrelativistic Hamiltonian connecting the two sets of  $e'$  orbitals