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Theory of translational diffusion in nematic liquid crystals*

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The theory of translational diffusion in nematic liquid crystals is developed from the standpoint of hydrodynamics and molecular-hydrodynamic interactions. The anisotropy of the diffusivity is obtained and related to the orientational order parameter, viscosity coefficients, and the detailed molecular geometry. Liquid-crystal hydrodynamics, Riemannian geometry, and molecular chain space are utilized in the theoretical development. The results for the diffusivity parallel and perpendicular to the director in p-azoxyanisole (PAA) at 125 °C are $D^{\parallel} = 4.3 \times 10^{-6}$ and $D^{\perp} = 3.1 \times 10^{-6}$ cm^2/sec, respectively, giving an anisotropy ratio $D^{\parallel}/D^{\perp} = 1.4$. In addition, the temperature dependence of $D^{\perp}$ is obtained, using available viscosity data. $D^{\perp}$ ($D^{\parallel}$) shows an increase (decrease)—corresponding to the decrease in order parameter—as the isotropic transition temperature is approached.

The velocity autocorrelation function has recently been solved in isotropic liquids through the utilization of projection-operator techniques developed by Mori[1] and Zwanzig.[2] The memory kernel in this type of formalism was investigated by Rice[3] and by Corngold and Duderstadt[4] using a perturbation expansion in isotropic liquids. A theory based on a frequency-dependent friction constant which utilized fluctuation-dissipation theorems, dispersion relations, and sum rules was applied by Martin and Yip[5] to make a comparison of the theory for self-diffusion in argon with the computer results of Rahman.[6] A consideration of liquid-crystal symmetries, potentials, and frequency dispersion relations reveals that the requisite modifications of the theories which have been mentioned are not trivial when applied to anisotropic fluids. This author mentioned an attempt to modify the theory of Martin and Yip[5] for application to self-diffusion in nematic liquid crystals and, in addition, presented the results of calculations which utilized a modified Kirkwood theory.[7] A proper formulation for a kinetic-equation approach would involve obtaining solutions to a generalized kinetic equation, including both translation and rotational motions, for liquid-crystal phase symmetries. Then the translational self-diffusion coefficients would be given by the velocity autocorrelation function:

$$D_{ij} = \int_0^{\infty} dt \, \langle v_i(t) v_j(0) \rangle = m^{-2} \int_0^{\infty} dt \int \cdots \int d^3k_0 \, d^6\xi \, d^6\xi_0 \, p_i \, G_{0\vec{\kappa}_0}(\vec{k}=0, \xi, \vec{k}_0, \vec{\xi}_0, t) \, p_{0j} f^{(1)}_{\vec{\kappa}_0}(\vec{k}_0, \xi_0) \,, \tag{1}$$

where $\vec{\xi} = (\vec{p}, \vec{\omega})$ and t, $\vec{k}, \vec{p}$, and $\vec{\omega}$ are time, wave vector, linear momentum, and angular velocity, respectively. G, $\vec{\kappa}$, and f represent the correlation function, Euler-angle representation, and single-particle distribution function, respectively. A similar equation can be written to represent rotational-velocity autocorrelations. If solutions to the generalized kinetic equation can be obtained then the diffusivity-tensor components can be written from a knowledge of the intermolecular potential.[8] However, the complexity is such that considerable time will be required in order to obtain solutions and evaluate the results.

Another simpler method has been reported by Chu and Moroi[8] in which the self-diffusion coefficients and their anisotropy ratio are calculated from a parametrized form of the momentum autocorrelation function utilizing a molecular-clustering assumption.

An ancillary theoretical approach to the problem of diffusion in liquid crystals is one which deals not with the basic calculation of the velocity autocorrelation functions but with the characteristics of the diffusion process and its molecular parameters. The utility of such a theory derives from the variety of influences affecting molecular migration in these systems. These influences and characteristics include the following: anisotropy, effects of the detailed molecular geometry, temperature, and orientational and translational order parameters. The potential applications of a theoretical approach which includes these characteristics are the prediction of the diffusivity components and the effects of orientational and/or translational order parameters in the nematic, smectic, cholesteric, and lyotropic mesophases. In addition, potentially useful applications of the theory are in studies of mass transport in living systems such as biological membranes and other groupings of axially ordered molecules in biosystems.

The basic reference for the theoretical background for this research in Oseen's hydrodynamic theory[9] which was developed for isotropic fluids. In that theory a hydrodynamic interaction tensor was introduced and the effects of hydrodynamic interaction with special three-dimensional shapes was studied. The Oseen tensor stems from singgular solutions to the Navier-Stokes equation. Subsequently, Kirkwood[10] modeled a tensor approach to the diffusion of macromolecules in aqueous solutions such that effects of the perturbation on the velocity of a molecular segment by the Oseen hydrodynamic interaction tensor were incorporated within the diffusivity. In addition, an accounting was made of the many-body aspects and of the possible generalized coordinates of large organic molecules. Molecular-chain space was utilized and the tensor properties of the molecular solution of the diffusivity were incorporated in the metric and Oseen tensors. In the Kirkwood and the present theory the diffusivity tensor components are given by

$$D^{\alpha\beta} = kT(g^{\alpha\beta}/\zeta + T^{\alpha\beta}) , \tag{2}$$

where $g^{\alpha\beta}$ and $T^{\alpha\beta}$ are the metric and Oseen tensors, respectively, and ζ is the scalar friction constant.

In Kirkwood's theory the viscosity was assumed to be a scalar; the theory was not derived for anisotropic fluids such as liquid crystals. In addition, Kirkwood's theory assumed all segments of the molecule to be identical and did not consider effects of orientational or translational order-disorder. The Kirkwood theory is also ineffectual in treating rotational diffusion in anisotropic fluids since the derivation on which it is based is the Navier-Stokes equation for linear motion rather than the angular-motion analog. The Kirkwood theory was designed, and was very successful, for the Brownian motion of macromolecules such as polymers in an isotropic matrix. The present theoretical derivation is done for self-diffusion for liquid-crystal order and makes use of the recent hydrodynamic theory of Jähnig and Schmidt[11] for nematic liquid crystals together with the Oseen-Kirkwood approach to molecular-hydrodynamic interactions.

The initial experimental work on diffusion in liquid crystals, done by Svedberg[12] in 1918, showed that for impurity diffusion in nematic mixtures $D^{\parallel} > D > D^{\perp}$, where $D^{\parallel}$ and $D^{\perp}$ represent the diffusivities parallel and perpendicular to an aligning magnetic field of 3 kG. Subsequently, Blinc *et al.*[13] reported order-of-magnitude measurements of the self-diffusion in *p*-azoxyanisole (PAA). Yun and Frederickson,[14] utilizing radio-tracer techniques, found a maximum anisotropy ratio $D^{\parallel}/D^{\perp}$ of approximately 1.3 and reported the temperature dependence of $D^{\parallel}$, D^0, and $D^{\perp}$, where D^0 is the diffusivity of a nonaligned, disoriented nematic over the nematic range of PAA. In addition, phase-transition effects indicative of a change in the order parameter were found in the temperature dependence of $D^{\parallel}$ and $D^{\perp}$ as the clearing temperature T_c was approached. Additional work on the anisotropy and its temperature dependence in PAA has been reported[15] utilizing quasielastic neutron scattering. The results of this technique, however, may include rotational diffusion effects.

In the room-temperature nematic *p*-methoxybenzylidene-*p'*-*n*-butylaniline (MBBA), Murphy and Doane[16] have found the anisotropy of impurity diffusion (tetramethylsilane, TMS) to be very small. Additional impurity-diffusion results have been obtained recently by Rondelez[17] for dye molecules in MBBA which indicate that $D^{\parallel}/D^{\perp} = 1.6$–1.7. Zupancic *et al.*[18] have recently found, using a multiple-pulse NMR spin-echo technique, a ratio of $D^{\parallel}/D^{\perp} = 1.4$ for self-diffusion in MBBA and postulated a value of 2.2 for *perfectly* ordered MBBA.

The need for the inclusion of the effects of *translational* order in a theory for smectic liquid crystals is suggested by the finding[19] that $D^{\perp} \simeq 10D^{\parallel}$ for diffusion of TMS in smectic *A* and *B* 4-*n*-butoxybenzylidene-4'-*n*-octylaniline. Doane[20] has found that $D^{\perp}/D^{\parallel}$ for *self-diffusion* in this compound is much less, however. In a study of the homologous nematic series which includes MBBA Doane also found that $D^{\perp}/D^{\parallel} > 1$ in the member of the series which is closest to the smectic phase while $D^{\parallel}/D^{\perp} > 1$ for other members. The former finding may indicate an effect of short-range smectic order in the nematic matrix.

In cell membranes and liquid bilayers there is evidence[21] which indicates that smectic modeling and liquid-crystal-type diffusion processes are relevant. Therefore, certain of the experimental and theoretical results for liquid crystals may be useful in membrane research.

In the succeeding sections the theoretical development will be presented, numerical analysis and interpretation given, and a comparison will be made with experimental results for PAA. The Riemannian geometry which is utilized is necessitated by the use of generalized molecular coordinates in *N*-dimensional molecular-chain space.

HYDRODYNAMIC THEORY

The relationship between hydrodynamic theory of fluid motion and molecular diffusion stems from the theory of Brownian motion by Einstein.[22] The incorporation of the theory which has evolved for isotropic liquids[9, 10] in the more complex structure of liquid-crystal theory is facilitated by the hydrodynamic theory of nematic liquid crystals given by Jähnig and Schmidt.[11] We begin, therefore, by writing the symmetric stress tensor[11] for viscous flow in component form:

$$\pi^{\alpha\beta} = -\eta^{\alpha\beta}{}_{\gamma\delta}A^{\gamma\delta} - \eta^{\alpha\beta}{}_{\gamma}N^{\gamma} , \tag{3}$$

where

$$\begin{aligned} A^{\gamma\delta} &= \tfrac{1}{2}\vec{a}^{\gamma}\cdot(\vec{a}_k \nabla_l v^k \vec{a}^l + \vec{a}^k \nabla_k v^l \vec{a}_l)\cdot\vec{a}^{\delta} \\ &= \frac{1}{2}\left(\frac{\partial\dot{q}^{\delta}}{\partial q_{\gamma}} + \frac{\partial\dot{q}^{\gamma}}{\partial q_{\delta}} + \frac{\partial g^{\gamma\delta}}{\partial q^m}\dot{q}^m\right) , \end{aligned} \tag{4}$$

$$N^{\gamma} = \vec{a}^{\gamma}\cdot(\vec{a}_k\Omega^k - \tfrac{1}{2}a_k\epsilon^{k\mu\nu}\nabla_{\mu}v_{\nu}) . \tag{5}$$

In Eq. (4), $\vec{a}_i$ is given by a sum in molecular-chain space for a molecule with an odd number of segments,[23]

$$\vec{a}_i = \sum_{l=-n}^{n} \frac{\partial\vec{R}^l}{\partial q^i} , \tag{6}$$

and $\vec{a}^i = g^{ij}\vec{a}_j$, where g^{ij} is the contravariant metric tensor. $\vec{R}^l$ is a spatial vector denoting the position of the lth segment and q^i is the ith generalized molecular coordinate. In Eq. (3) the viscosity tensors for translational and rotational motion are denoted by $\eta^{\alpha\beta}_{\gamma\delta}$ and $\eta^{\alpha\beta}_{\gamma}$, respectively, and in Eqs. (4) and (5) $\vec{v}$ and $\vec{\Omega}$ are the linear and angular velocities, respectively.

In the subsequent development of the theory the covariant derivatives of $A^{\gamma\delta}$ and N^{γ}, which are given by

$$\begin{aligned} A^{\gamma\delta}{}_{,\beta} = \frac{1}{2}\Bigg(&\frac{\partial^2\dot{q}^{\delta}}{\partial q^{\beta}\partial q_{\gamma}} + \frac{\partial^2\dot{q}^{\gamma}}{\partial q^{\beta}\partial q_{\delta}} + \frac{\partial g^{\gamma\delta}}{\partial q^m}\frac{\partial\dot{q}^m}{\partial q^{\beta}} \\ &+ \dot{q}^m\frac{\partial^2 g^{\gamma\delta}}{\partial q^{\beta}\partial q^m}\Bigg) , \end{aligned} \tag{7}$$

$$N^{\gamma}{}_{,\beta} = \frac{\partial\Omega^{\gamma}}{\partial q^{\beta}} + \{j\,\beta,\gamma\}\Omega^j - \tfrac{1}{2}(\epsilon^{\gamma\mu\nu}\nabla_{\mu}v_{\nu})_{,\beta} , \tag{8}$$

will be needed. Following Oseen[9] we choose to write a scalar equation, utilizing two different velocities, $\vec{v}$ and $\vec{u}$, integrated over the system's volume. We let a bar denote the use of $\vec{v}$ in $\overleftrightarrow{A}$ and $\vec{N}$, whereas the unbarred forms involve $\vec{u}$, and a bar over $\overleftrightarrow{\pi}$ denotes the stress tensor for velocity $\vec{v}$. The scalar equation is written as

$$\begin{aligned} \int_V \{&v_{\alpha}(\eta^{\alpha\beta}{}_{\gamma\delta}A^{\gamma\delta}{}_{,\beta} + \eta^{\alpha\beta}{}_{\gamma}N^{\gamma}{}_{,\beta} + \pi^{\alpha\beta}{}_{,\beta}) \\ &- u_{\alpha}(\eta^{\alpha\beta}{}_{\gamma\delta}\bar{A}^{\gamma\delta}{}_{,\beta} + \eta^{\alpha\beta}{}_{\gamma}\bar{N}^{\gamma}{}_{,\beta} + \bar{\pi}^{\alpha\beta}{}_{,\beta})d\tau\} = 0, \end{aligned} \tag{9}$$

where $v^{\beta} = \dot{q}^{\beta}$, $\vec{v} = \vec{a}_{\alpha}\dot{q}^{\alpha}$, and $v_{\alpha} = g_{\alpha\beta}v^{\beta}$. We define

$$\Psi^{\alpha\beta} \equiv \eta^{\alpha\beta}{}_{\gamma\delta}A^{\gamma\delta} + \eta^{\alpha\beta}{}_{\gamma}N^{\gamma} + \pi^{\alpha\beta} , \tag{10}$$

$$\Phi^{\beta}{}_{,\beta} \equiv (v_{\alpha}\Psi^{\alpha\beta})_{,\beta} , \tag{11}$$

and use these definitions to rewrite Eq. (9) as

$$\int_V (\Phi^{\beta}{}_{,\beta} - \bar{\Phi}^{\beta}{}_{,\beta})d\tau - \int_V (v_{\alpha,\beta}\Psi^{\alpha\beta} - u_{\alpha,\beta}\bar{\Psi}^{\alpha\beta})d\tau = 0. \tag{12}$$

Invoking Green's theorem the first term in Eq. (12) becomes

$$\int_S (\Phi^{\beta}n_{\beta} - \bar{\Phi}^{\beta}n_{\beta})dS \tag{13}$$

so that Eq. (12) can be written out as

$$\int_S \{v_{\alpha}(\eta^{\alpha\beta}{}_{\gamma\delta}A^{\gamma\delta} + \eta^{\alpha\beta}{}_{\gamma}N^{\gamma} + \pi^{\alpha\beta})n_{\beta} - u_{\alpha}(\eta^{\alpha\beta}{}_{\gamma\delta}\bar{A}^{\gamma\delta} + \eta^{\alpha\beta}{}_{\gamma}\bar{N}^{\gamma} + \bar{\pi}^{\alpha\beta})n_{\beta}\}\,dS - \int_V (v_{\alpha,\beta}\Psi^{\alpha\beta} - u_{\alpha,\beta}\bar{\Psi}^{\alpha\beta})d\tau = 0. \tag{14}$$

Following the initial development by Oseen[9] and subsequent adaptation by Kirkwood[10] to molecular-chain space we write the interaction tensor

$$\begin{aligned} t^{\alpha\xi}_{ls} = \frac{g^{\alpha\sigma}g^{\xi\tau}}{|\vec{R}_{ls}|}\Bigg[&\frac{\partial\vec{R}_l}{\partial q^{\sigma}}\cdot\frac{\partial\vec{R}_s}{\partial q^{\tau}} \\ &+ \frac{1}{R^2_{ls}}\left(\vec{R}_{ls}\cdot\frac{\partial\vec{R}_l}{\partial q^{\sigma}}\right)\left(\vec{R}_{ls}\cdot\frac{\partial\vec{R}_s}{\partial q^{\tau}}\right)\Bigg], \end{aligned} \tag{15}$$

where the indices l and s refer to molecular segments and $\vec{R}_{ls}$ is the vector distance between the segments l and s. This tensor differs from Kirkwood's $\overleftrightarrow{T}$ by a factor $(8\pi\eta)^{-1}$ since the anisotropic analog of this term will enter the theory naturally [from the viscosity tensors in Eq. (14)]. The tensor components summed over molecular segments are given by $t^{\alpha\beta} = \sum t^{\alpha\beta}_{ls}$. In the nematic case $\overleftrightarrow{t}$ differs from Kirkwood's $\overleftrightarrow{t}$ through the presence of the order parameter S, which relates the orientations of the molecules in Eq. (15). The result of incorporating S in $\overleftrightarrow{t}$ is shown in Eq. (31).

We use $\overleftrightarrow{t}$, as defined by Eq. (15), which is the counterpart to that used by Oseen in an analogous manner, as a replacement for $\vec{v}$, which alters the fundamental character of Eq. (14). Before making this transformation, however, we digress briefly to give a physical picture of the relative velocities involved in the hydrodynamic interactions between molecular segments and their surroundings and of the assumptions made. The role of the molecular-hydrodynamic interaction tensor $\overleftrightarrow{T}$ which includes $\overleftrightarrow{t}$ in the weaving together of hydrodynamic and molecular theory will also become manifest in the following development.

We consider the velocity of the matrix fluid at the position of a particular molecular segment l as $\vec{\mathbf{u}}_l$, and $\vec{\mathbf{u}}_l^0$ as the unperturbed fluid velocity, in the absence of segment l. Another velocity, $\vec{v}_l$, is the velocity of segment l with respect to a laboratory reference frame. Then we let

$$\vec{u}_l = \vec{\mathbf{u}}_l^0 - \vec{\mathbf{u}}_l \ , \tag{16a}$$

$$\vec{w}_l = \vec{u}_l - \vec{v}_l \ , \tag{16b}$$

$$\vec{F}_l \sim -\zeta \vec{w}_l \ , \tag{16c}$$

where ζ is the friction constant and where $\vec{u}_l$ is the perturbation of the velocity caused by hydrodynamic interactions and is given at a general point p, due to a force acting at q, by

$$\vec{u}(\vec{r}_p) = \overleftrightarrow{T}(\vec{r}_{pq}) \cdot \vec{F}(\vec{r}_q) \ . \tag{17}$$

The velocities in molecular-chain space are given by $\vec{u} = \sum \vec{u}_l$.

The velocity $\vec{v}$ in Eq. (14) is now replaced by $\overleftrightarrow{t}$ with the resultant transformation from a scalar to a vector equation. The surface integral is divided into inner and outer integrals such that $\int_S \to \int_\gamma + \int_\Gamma$, where γ is the surface of a small sphere of radius r. Γ is the surface of the system whose hydrodynamic interactions are being considered. Then the quasistatic assumptions, which are analogous to those invoked by Oseen,[9] are adopted in which the integrals over u_i, $u_{i,j}$, $t_{ik,j}$, and Ω_i all vanish or become negligibly small on the outer surface Γ and in the intervening volume V between γ and Γ.

A basis for these conditions is that the *relative* motion between surfaces γ and Γ contributes in a hydrodynamic fashion with a solidlike rigidity between. In a single large molecule, hydrodynamic-like interactions occur on the outer surfaces of each segment[10] and π^{ij} behaves in a manner analogous to a surface traction acting on Γ. These conditions make the problem tractable in both the isotropic and anisotropic cases; the anisotropy of the medium does not give rise to insoluble terms. The relationship of these conditions to localized fluctuations in kinetic variables, which give rise to Brownian motion of a molecule relative to its surroundings, is apparent when the magnitudes of local and nonlocal terms are examined. Under these assumptions the nonvanishing terms of Eq. (14) give

$$\int_\Gamma t_\alpha^\xi \pi^{\alpha\beta} n_\beta \, dS + \int_\gamma \{ t_\alpha^\xi (\eta^{\alpha\beta}{}_{\gamma\delta} A^{\gamma\delta} + \eta^{\alpha\beta}{}_\gamma N^\gamma + \pi^{\alpha\beta}) n_\beta - u_\alpha (\eta^{\alpha\beta}{}_{\gamma\delta} \bar{A}^{\gamma\delta\xi} + \eta^{\alpha\beta}{}_\gamma \bar{N}^{\gamma\xi} + \bar{\pi}^{\alpha\beta\xi}) n_\beta \} \, dS = 0, \tag{18}$$

where $t_\alpha^\xi = g_{\alpha\beta} t^{\beta\xi}$.

When we let $\int dS \to 4\pi r^2$ and note that $t^{\beta\xi} \sim r^{-1}$ we find that the product of t_α^ξ with the three terms in the first parentheses under the integral over γ all vanish when $r \to 0$. In addition, the $\bar{\pi}^{\alpha\beta\xi}$ and $\bar{\Omega}^{\gamma\xi}$ terms in the second parentheses also vanish thus leaving

$$\int_\Gamma t_\alpha^\xi \pi^{\alpha\beta} n_\beta dS = \lim_{r \to 0} \int_{4\pi r^2} u^\alpha (\eta^{\alpha\beta}{}_{\gamma\delta} \bar{A}^{\gamma\delta\xi} + \eta^{\alpha\beta}{}_\gamma \bar{N}^{\gamma\xi}) n_\beta dS \ . \tag{19}$$

The outer surface integral in Eq. (19) yields $t_\alpha^\xi F^\alpha$ and it is this term, together with the viscosity terms, which comprise the right-hand side of Eq. (17). This is shown clearly in Eqs. (26) and (27).

Before Eq. (19) is developed further the variables which appear in this equation will be considered. The divergence of $\overleftrightarrow{t}$ is given by

$$\vec{\nabla} t^{\to\xi} = \vec{a}^i \vec{a}_\alpha \left(\frac{\partial t^{\alpha\xi}}{\partial q^i} + \{ik, \alpha\} t^{k\xi} \right) , \tag{20}$$

which yields

$$t^{\delta\xi,\gamma} = \vec{a}^\gamma \cdot \vec{\nabla} t^{\to\xi} \cdot \vec{a}^\delta = \frac{\partial t^{\delta\xi}}{\partial q_\gamma} + \frac{1}{2} \frac{\partial g^{\gamma\delta}}{\partial q^k} t^{k\xi} \ . \tag{21}$$

The resulting form of $\bar{A}^{\gamma\delta\xi}$ is

$$\bar{A}^{\gamma\delta\xi} = \frac{1}{2} \left(\frac{\partial t^{\delta\xi}}{\partial q_\gamma} + \frac{\partial t^{\gamma\xi}}{\partial q_\delta} + \frac{\partial g^{\gamma\delta}}{\partial q^k} t^{k\xi} \right) \ . \tag{22}$$

The interaction tensor utilizing Eq. (15) can be written as

$$\begin{aligned} t^{\alpha\xi} &= \sum_{l \neq s} t_{ls}^{\alpha\xi} \\ &= \sum_{l \neq s} \frac{g^{\alpha\sigma} g^{\xi\tau}}{|\vec{R}_{ls}|} \left(\delta_{\sigma\tau} + \frac{R_\sigma^{ls} R_\tau^{ls}}{R_{ls}^2} \right) \\ &= \mu^{-2} \sum \left(\frac{\delta^{\alpha\xi}}{|\vec{R}_{ls}|} + \frac{R_{ls}^\alpha R_{ls}^\xi}{|R_{ls}^3|} \right), \end{aligned} \tag{23}$$

in which $g^{ij} = \delta^{ij}/\mu$ (see Appendix). The partial of $\overleftrightarrow{t}$ with respect to a spatial coordinate yields

$$\frac{\partial t_{ls}^{\alpha\xi}}{\partial R_\gamma^{ls}} = - \frac{R_{ls}^\gamma}{|\vec{R}_{ls}|^3} \left(\delta^{\alpha\xi} + 3 \frac{R_{ls}^\alpha R_{ls}^\xi}{R_{ls}^2} \right) \tag{24}$$

for deformable molecules.

Returning to the integration of Eq. (19) the $t^{k\xi} \partial g^{\gamma\delta} / \partial q^k$ will be omitted since it vanishes. Also, since the $\bar{\Omega}^{\gamma\xi}$ term, which is the analog of the local rotation velocity when $\vec{v}$ is replaced by $\overleftrightarrow{t}$, in $\bar{N}^{\gamma\xi}$ vanishes in the limit as $r \to 0$ after integration, it will be omitted. A short derivation, using Eqs. (20)–(24) in Eq. (19) yields

$$t^{\xi}_{\alpha}F^{\alpha}=-\lim_{r\to 0}\int_{\gamma}\sum_{ls}\frac{u_{\alpha}}{|\vec{R}_{ls}|^3}\left\{\eta^{\alpha\beta}{}_{\gamma\delta}\left(R^{\gamma}_{ls}\delta^{\delta\xi}+R^{\delta}_{ls}\delta^{\gamma\xi}+6\frac{R^{\gamma}_{ls}R^{\delta}_{ls}R^{\xi}_{ls}}{R^2_{ls}}\right)\right.$$
$$\left.+\eta^{\alpha\beta}{}_{\gamma}\epsilon^{\gamma}{}_{\mu\nu}\left(R^{\mu}_{ls}\delta^{\nu\xi}+R^{\nu}_{ls}\delta^{\mu\xi}+6\frac{R^{\mu}_{ls}R^{\nu}_{ls}R^{\xi}_{ls}}{R^2_{ls}}\right)\right\}n_{\beta}\,dS\ . \qquad (25)$$

Integrating Eq. (25) and taking the sum, we obtain

$$g_{\alpha\beta}t^{\beta\xi}F^{\alpha}=-2\pi u_{\alpha}\{\eta^{\alpha\beta}{}_{\gamma\delta}(n^{\gamma}\delta^{\delta\xi}+n^{\delta}\delta^{\gamma\xi}+6n^{\gamma}n^{\delta}n^{\xi})+\eta^{\alpha\beta}{}_{\gamma}\epsilon^{\gamma}{}_{\mu\nu}(n^{\mu}\delta^{\nu\xi}+n^{\nu}\delta^{\mu\xi}+6n^{\mu}n^{\nu}n^{\xi})\}n_{\beta}\ , \qquad (26)$$

where the n^i are unit-vector components which stem from the limit as $r\to 0$. Therefore, the perturbed velocity attributable to the hydrodynamic interactions with molecular segments is given by

$$u^{\beta}=-T^{\beta}_{\alpha}F^{\alpha}\ , \qquad (27)$$

where

$$T^{\beta}_{\alpha}=t^{\beta\xi}/2\pi\{\eta^{\alpha\sigma}{}_{\gamma}{}^{\xi}n^{\gamma}+\eta^{\alpha\sigma\xi}{}_{\delta}n^{\delta}+6\eta^{\alpha\sigma}{}_{\gamma\delta}n^{\delta}n^{\gamma}n^{\xi}+\eta^{\alpha\sigma}{}_{\gamma}(\epsilon^{\gamma}{}_{\mu}{}^{\xi}n^{\mu}+\epsilon^{\gamma\xi}{}_{\nu}n^{\nu}+6\epsilon^{\gamma}{}_{\mu\nu}n^{\mu}n^{\nu}n^{\xi})\}\ n_{\sigma} \qquad (28)$$

is the complete molecular-hydrodynamic interaction tensor, including the viscosity tensors, which is the anisotropic analog of that given by Kirkwood.[10] Utilizing the symmetry of the viscosity coefficients[11] we write the contravariant form of $\overleftrightarrow{T}$ as

$$T^{\alpha\beta}=t^{\alpha\xi}/4\pi\{\eta_{\beta}{}^{\sigma}{}_{\gamma}{}^{\xi}n^{\gamma}+3\eta_{\beta}{}^{\sigma}{}_{\gamma\delta}n^{\delta}n^{\gamma}n^{\xi}$$
$$+\eta_{\beta}{}^{\sigma}{}_{\gamma}(\epsilon^{\gamma}{}_{\mu}{}^{\xi}n^{\mu}+3\epsilon^{\gamma}{}_{\mu\nu}n^{\mu}n^{\nu}n^{\xi})\}n_{\sigma}\ . \qquad (29)$$

The symmetry of the nematic phase and the incompressibility condition lead to the reduction of the number of nonvanishing independent viscosity components to five for η_{ijkl} and one for η_{ijk}.

The form of the diffusivity tensor which will be used is that derived initially by Kirkwood[10] and is given by

$$D^{\alpha\beta}=kT(g^{\alpha\beta}/\zeta+T^{\alpha\beta})\ . \qquad (30)$$

The symmetry of transversely isotropic materials shows that $D^{xx}=D^{yy}$ and $D^{ij}=0$ for $i\neq j$. An actual numerical evaluation of our results shows that the off-diagonal terms in $\overleftrightarrow{D}$ are negligible and that the diagonal components display the expected symmetry. Consequently, only two nonvanishing independent components of $\overleftrightarrow{D}$ require evaluation and these are $D^{\parallel}=D^{zz}$ and $D^{\perp}=D^{xx}=D^{yy}$, where $\parallel$ and $\perp$ denote components parallel and perpendicular to the director, respectively. When thermal averaging is considered the orientational order parameter enters the second term in Eq. (24) via $\langle\sin^2\theta\rangle=\frac{2}{3}(1-S)$, where S is the order parameter. Then

$$t^{\parallel}=\sum_{ls}\frac{2(2+S)}{3|\vec{R}_{ls}|}\ ,\quad t^{\perp}=\sum_{ls}\frac{5-2S}{3|\vec{R}_{ls}|}\ . \qquad (31)$$

In the Jähnig-Schmidt notation[11] the diffusivity components are given by

$$D^{\parallel}=kT\left(\frac{1}{\mu\zeta}+\frac{2+S}{6\pi\mu^2\phi}\Big/(6\eta_3+3\tfrac{1}{2}\eta_4+4\eta_5)\right)\ , \qquad (32a)$$

$$D^{\perp}=kT\left(\frac{1}{\mu\zeta}+\frac{5-S}{12\pi\mu^2\phi}\Big/(7\eta_1+8\eta_2+3\eta_3+\tfrac{7}{4}\eta_4)\right), \qquad (32b)$$

where $\phi^{-1}=\sum 1/|\vec{R}_{ls}|$ (see Appendix for evaluation). The transformation between the Jähnig-Schmidt[11] and Erickson[24]-Leslie[25] viscosity coefficients is given in Table I (a). Utilizing this code we obtain the diffusivity components in Leslie-Erickson notation:

$$D^{\parallel}=kT\left(\frac{1}{\mu\zeta}+\frac{2+S}{6\pi\mu^2\phi}\Big/(4\alpha_1+\tfrac{3}{2}\alpha_2+\tfrac{13}{2}\alpha_3+6\alpha_4+10\alpha_5)\right), \qquad (33a)$$

$$D^{\perp}=kT\left(\frac{1}{\mu\zeta}+\frac{5-S}{12\pi\mu^2\phi}\Big/(-\tfrac{11}{4}\alpha_2+\tfrac{9}{4}\alpha_3+6\alpha_4-\tfrac{3}{2}\alpha_5)\right). \qquad (33b)$$

A third form of the diffusivities can be written using the coefficients η_1', η_2', and η_3' of Meisowicz,[26] the Orsay Liquid Crystal Group,[27] and Papoular[28] as given in Table I (b). This form is useful in the numerical evaluation of the temperature dependence of $\overleftrightarrow{D}$ for PAA since the temperature-dependent viscosity data which are available are in this form. From the code of Table I (b) the parentheses in the denominators of Eqs. (33) become

$$4\alpha_1+8\alpha_3+20\eta_2'-8\eta_3'-11\tfrac{1}{2}\gamma_1\ , \qquad (34a)$$

TABLE I(a). The translation code between the viscosity coefficients of Jähnig and Schmidt (Ref. 11) and those of Erickson (Ref. 24) and Leslie (Ref. 25) as communicated by Jähnig (Ref. 34). We note that $\gamma_2=\alpha_6-\alpha_5$ and that $\gamma_1=\alpha_3-\alpha_2$.

$\eta_1=-\frac{1}{2}(\alpha_2+\alpha_5)$	$\eta_4=2(\alpha_4+\alpha_5)+\gamma_2$
$\eta_2=\frac{1}{2}\alpha_4$	$\eta_5=\frac{1}{2}(2\alpha_1+\alpha_2+2\alpha_3+\alpha_4+3\alpha_5)$
$\eta_3=-\frac{1}{2}(\alpha_2+\alpha_4+\alpha_5)$	$\nu=-\gamma_2$

$$\tfrac{17}{4}\gamma_1 - \tfrac{1}{2}\alpha_3 - 3\eta_2' + 15\eta_3' \ , \tag{34b}$$

where primes are used to distinguish these coefficients from those of Jähnig and Schmidt.

In the isotropic case the translational viscosity η_{ij}^{kl} is given by[29]

$$\eta_{ij}^{kl} = \eta(\delta_i^k \delta_j^l + \delta_i^l \delta_j^k - \tfrac{2}{3}\delta_{ij}\delta^{kl}) \ , \tag{35}$$

where η is the shear viscosity of isotropic liquids. In this case, it can be shown, by referring to the theory presented above, that all but the first viscosity term in the denominator of Eq. (29) vanish. This term, given by Eq. (35), reduces, for $\beta = \xi$ and σ, γ summed in Eq. (29), to $3\tfrac{1}{3}\eta$ and gives a value of $13\tfrac{1}{3}\pi\eta$ for the denominator of Eq. (29). In the isotropic case $S = 0$ and a factor of $\tfrac{4}{3}$ stems from $\overleftrightarrow{t}$ which appears in the numerator of Eq. (29) and which gives rise to the $(8\pi\eta)^{-1}$ dependence of $\overleftrightarrow{T}$ given by Kirkwood.[10] The details of the exact reduction of the theory to that for isotropic symmetry are a bit more complex but the argument presented here is sufficient to indicate the comparison. However, it is known that all α_i in Eqs. (33) vanish in the isotropic case except α_4. Then the viscosity terms in $D^{\parallel}$ and $D^{\perp}$ are identical, as one would expect. It is not known, however, why $D^{\parallel}$ and $D^{\perp}$ are not equal when $S = 0$ in Eqs. (33), since this is expected in these equations without reverting back to the original derivation of D and making everything isotropic to begin with.

NUMERICAL EVALUATION FOR PAA

There are five independent viscosity coefficients in Eqs. (32), (33), or (34) which are required, together with their temperature dependence across the nematic range, for numerical evaluation of $\overleftrightarrow{D}$. Unfortunately, reliable temperature-dependent data are not available for all five coefficients for any nematic. However, the Orsay Group[27] has obtained the Leslie-Erickson coefficients at 125°C for PAA. We use these coefficients, together with the values of μ and ϕ from the Appendix. The value of ξ is obtained from the data of Yun and Fredrickson[14] utilizing the same procedure used before.[7] The order parameter of Glarum and Marshall[30] is used. Then $D^{\parallel}(125\,°\mathrm{C}) = 4.3 \times 10^{-6}\ \mathrm{cm^2/sec}$ and $D^{\perp}(125\,°\mathrm{C}) = 3.1 \times 10^{-6}\ \mathrm{cm^2/sec}$, giving an anisotropy ratio $D^{\parallel}/D^{\perp} = 1.4$. This compares to the experimental values of Yun and Fredrickson[14] at the same temperature, which are $D^{\parallel} = 4.1 \times 10^{-6}\ \mathrm{cm^2/sec}$, $D^{\perp} = 3.2 \times 10^{-6}\ \mathrm{cm^2/sec}$, and $D^{\parallel}/D^{\perp} = 1.3$. The temperature dependence of $D^{\perp}$ can be evaluated, since the $-\tfrac{1}{2}\alpha_3$ term in Eq. (34b) is negligibly small, through the utilization of the activation energies of η_2' and η_3' from Porter and Johnson[31] and of γ_1 from Meiboom and Hewitt.[32] This method utilizes a *consistent set* of viscosity data—that of the Orsay Group—and incorporates activation energies from other data. The latter is predicated on the principle that reliable activation energies are more easily obtained experimentally than are absolute values in rate-constant measurements. Table II lists the values of γ_1, η_2', and η_3' obtained in this manner together with S from Glarum and Marshall[30] at various temperatures. Figure 1 shows a comparison of the theoretical results with the experimental data of Yun and Fredrickson[14] for PAA. The degree of agreement between theory and experiment for $D^{\perp}$ over the nematic range and for the anisotropy ratio at 125 °C is pleasing. It is not

TABLE I(b). The viscosity coefficients of Meisowicz (Ref. 26) and others (Refs. 27, 28), where η_1', η_2', and η_3' refer to molecules being parallel to the flow, parallel to the velocity gradient, and perpendicular to both flow and velocity gradient, respectively.

$$\eta_1' = \tfrac{1}{2}(\alpha_3 + \alpha_4 + \alpha_6)$$

$$\eta_2' = \tfrac{1}{2}(\alpha_4 + \alpha_5 - \alpha_2)$$

$$\eta_3' = \tfrac{1}{2}\alpha_4$$

TABLE II. Values of the order parameter S from Ref. (30) and of the viscosity coefficients η_2', η_3', and γ_1 from Ref. 27 utilizing activation energies from Refs. 31 and 32.

T(°C)	S	η_2'	η_3'	γ_1
116	0.64	0.073	0.034	0.082
120	0.62	0.067	0.032	0.072
125	0.58	0.061	0.030	0.059
130	0.54	0.053	0.028	0.049
135	0.40	0.040	0.020	0.030

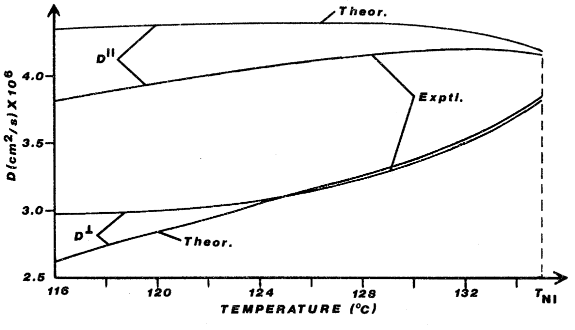

FIG. 1. Diffusivities parallel and perpendicular to the director, $D^{\parallel}$ and $D^{\perp}$, respectively, versus temperature in nematic p-azoxyanisole (PAA). The experimental data of Yun and Fredrickson (Ref. 14), which was obtained using the radio-isotope technique, is shown for comparison. The theoretical curves stem from Eqs. (33) and (34) using material constants (temperature dependent) given in Table II.

possible to evaluate the temperature dependence of $D^{\parallel}$ very accurately since α_1 and α_3 are not known except at 125 °C. Nevertheless, the general features of the experimental curve are obtained from the theory and the curves for $D^{\parallel}$ in Fig. 1 are in reasonable agreement.

DISCUSSION

The relationship between the diffusivity and the molecular friction constant or viscosity coefficient, which has been theoretically and experimentally verified in isotropic liquids, has never been shown for anisotropic liquids. Riseman and Kirkwood in Ref. 10 did, however, consider anisotropy in a limited sense; they considered anisotropy in $\vec{D}$ which was attributed to the anisotropy of the metric and hydrodynamic interaction tensors assuming perfectly aligned macromolecules in an isotropic matrix. In that theory no effect of the orientational order parameter or of an anisotropic matrix was considered. However, theoretical evaluation of both rotational and translational diffusivities was accomplished and found to correlate well with experimental observations. The present calculation has been done for anisotropic nematic-liquid-crystal order for translational diffusion. The rotational analog of this theory might best begin with the rotational counterpart to Eq. (3), which has been given by Jähnig and Schmidt[11] for nematic symmetry as

$$\epsilon_{ijk}\pi^{a}_{jk} = -\zeta_{ijk}A_{jk} - \zeta_{ij}N_j \; , \tag{36}$$

where π^{a}_{jk} is the antisymmetric stress tensor and ζ_{ijk} and ζ_{ij} are viscosity coefficients. An attempt was made in previous work[7] to relate rotational diffusion to the type of theory which is presented here but numerical evaluation gave results which did not correlate well with experimental observations in PAA. Therefore, a better approach is to begin with Eq. (36) and derive $\vec{D}_{\text{rot}}$ in a manner analogous to that done here for $\vec{D}_{\text{trans}}$. We note the presence of the cross-term tensors η_{ijk} and ζ_{ijk}, in Eqs. (3) and (36), respectively, and that these are equivalent when the Onsager relations are utilized—when axial vectors are replaced by antisymmetric tensors. (See Appendix B of Ref. 11.)

The sensitivity of Eqs. (32)–(34) for $D^{\parallel}$ and $D^{\perp}$ to the numerical values of the viscosity coefficients is dependent upon the signs, magnitudes, and numerical coefficients of the constituent coefficients. The sensitivity is quite significant; a 10% increase in γ_1, for example, results in a 20 and a 5% decrease in the hydrodynamic interaction portion of $D^{\parallel}$ and $D^{\perp}$, respectively. Consequently, since the experimental accuracy of γ_1, which is the coefficient which is most easily measured experimentally, is of the order of 5–7%,[32,33] the over-all uncertainty in the hydrodynamic interaction portion of $D^{\parallel}$ and $D^{\perp}$ using the available viscosity data is probably not much better than 50% for PAA. The relative magnitude of the g^{ij}/ζ and T^{ij} terms in $D^{\perp}$ ranges from 3:1 at 116°C to 1.5:1 at 135°C. Consequently, uncertainties in $D^{\perp}$ caused by uncertainties in T^{ij} increase as $T \to T_c$.

The effect of the temperature dependence of S on D as $T \to T_c$ is to decrease $D^{\parallel}$ and increase $D^{\perp}$, as can be seen in Eqs. (32) and (33). Effects which can be attributed to S have been observed experimentally in PAA as shown in Fig. 1 near T_c. In addition to the explicit dependence of T^{ij} on S the viscosities also display a dependence on S and deviate from logarithmic behavior as $T \to T_c$. This feature is taken into account in the calculated values of D.

In a first-order phase transition S does not go to 0 continuously and $D^{\parallel}$ and $D^{\perp}$ display discontinuities at T_c in the transition from the nematic to the isotropic phase. Since $D^{\parallel} > D^{\perp}$ the following condition obtains for the nematic phase even as $T \to T_c$:

$$\frac{2+S}{4\alpha_1 + 3\alpha_2/2 + 13\alpha_3/2 + 6\alpha_4 + 10\alpha_5} > \frac{5-S}{-11\alpha_2/4 + 9\alpha_3/4 + 6\alpha_4 - 3\alpha_5/2} \, . \tag{37}$$

The tendency which is observed in certain homologous series and nematic mixtures toward second-order phase-transition behavior will tend to bring Eq. (37) close to an equality as $T \to T_c$.

With regard to the complexities of this theory, which utilizes molecular-chain space and Reimannian geometry to describe rigid-molecule behavior, the effects of segment size on $\sum 1/|\vec{R}_{ls}|$ and $g_{\alpha\beta}$ are very significant. This can be seen in the Appendix. The significance of segment size on hydrodynamic interactions was not considered by Kirkwood[10] since he assumed identical segments. Segment sizes determine the lengths between which hydrodynamic interactions take place and these produce significant differences in the theory for different molecules. In addition, the utilization of generalized coordinates in molecular-chain space allows one to consider internal degrees of freedom.

The requisite modifications of the theory for application to smectic and lyotropic liquid crystals include the addition of the translational order parameter. The question of whether the anisotropy ratio can be greater or less than 1 in different smectics is an interesting question for considera-

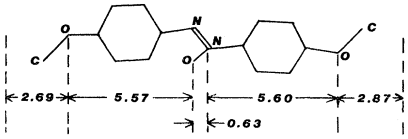

FIG. 2. Choice of segment lengths in PAA which are used in numerical evaluation of the molecular-hydrodynamic interaction tensors. The x-ray data of Ref. 35 were utilized to obtain the projected lengths on the molecular axis which are shown.

tion in this theory. Results so far have indicated that $D^{\perp} > D^{\parallel}$ for both self[20] and impurity[21] diffusion. If this result also obtains in smectic-type lipid bilayers and membranes it could have some significance in membrane transport considerations.

The molecular geometries of PAA and MBBA were very simply analyzed as shown in the Appendix. More complicated geometries, such as double-tailed molecules, can also be treated. With regard to membrane modeling, the type of approach developed here should be useful in the consideration of transport of specific molecules. For example, in the carrier mechanism the addition of certain ions to the carrier will affect the parameters μ and ϕ, which should be easily calculable. In addition, dipole effects which are needed for membrane calculations can be added to this theory following the initial concepts of Kirkwood[10] for treating molecular systems with permanent dipole moments. The analysis of the two factors which include effects of molecular geometries, given in the Appendix, assumes rigid linear molecules with the molecular-hydrodynamic interactions depending on segment size and spacing between segments. These assumptions are valid in first approximation for short molecules such as PAA and MBBA. However, for long flexible molecules the effects of both conformational changes and tail rotations on the diffusivity would be significant factors to consider.

APPENDIX: MOLECULAR SUMS FOR PAA

TABLE III. Segment lengths for the PAA molecule taken from bond lengths projected onto the molecular axis. See Fig. 2 and Ref. 35. The quantity $b = 5.15$ Å is an average of the molecular cross-section diameters, whereas b_l is the length of segment l.

Segment	Projected segment length b_l (Å)	 b_l/b
1	2.69	0.522
2	5.57	1.08
3	0.63	0.122
4	5.60	1.09
5	2.87	0.557

The evaluation of the molecular-segment sum given by

$$\sum_{\substack{l \neq s \\ -n}}^{+n} \frac{1}{|\vec{R}_{ls}|} \tag{38}$$

follows the general method introduced by Kirkwood[10] but involves an assignment of segment size, which is shown in Fig. 2. The bond lengths and angles are taken from Krigbaum *et al.*[35] for solid PAA; no significant differences are expected from these values for molecules in the nematic state. The segment lengths were calculated from the projected bond lengths on the molecular axis, which are given in Table III. The value of the sum obtained using the segment sizes given in Table III is 6.80×10^{8}/cm, which gives a value $\phi = 1.47 \times 10^{-9}$ cm.

The evaluation of the covariant metric tensor in molecular-chain space is based on the following form of the tensor:

$$g_{\alpha\beta} = \sum_{-n}^{n} \left(\frac{b_l}{b}\right)^2 \hat{e}_{\alpha}^{(l)} \cdot \hat{e}_{\beta}^{(l)} , \tag{39}$$

where $\hat{e}_i^{(l)}$ is the ith component of a unit vector for segment l (for $2n+1$ segments). The length of the lth segment is b_l and the average of the molecule's cross-section diameters is given by b. The quantity b_l/b is given in the third column of Table III. For PAA the value of the coefficient μ is 2.954. The contravariant metric tensor is given by $g^{\alpha\beta} = \delta^{\alpha\beta}/\mu = 0.339\delta^{\alpha\beta}$.

In MBBA a similar calculation yields $\phi = 1.41 \times 10^{-9}$ cm and $\mu = 3.14$.

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