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Molecular Crystals and Liquid Crystals

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Diffusion Theory in Liquid Crystals†

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Abstract—An adaptation of liquid and solid state diffusion theory is made here to diffusion in liquid crystals. Kirkwood's diffusion theory is modified to take into account anisotropic viscosity, molecular order and the detailed geometry of the molecules. For *p*-azoxyanisole the diffusivities parallel and perpendicular to the director are 4.25×10^{-6} and 2.87×10^{-6} cm²/s, respectively, at 122°C which are very close to experimental values and which give the ratio $D^{\parallel}/D^{\perp} = 1.48$. The unmodified Kirkwood theory gives a ratio of 3.0 which is more than twice the experimental value. The rotational diffusivity in PAA is $D_r = 6.95 \times 10^8$/s and during the time D_r^{-1} the translational motion perpendicular to the director is 6.4Å in the modified Kirkwood theory, which indicates a coupling between translational and rotational motion. In addition, $D^{\parallel}$ is found inversely proportional to molecular length. An analysis of the temperature dependence of D indicated that $\mathrm{d}D/\mathrm{d}T$ could not vanish over a 20°C temperature range if usual activation energies for translation and rotation in liquids are considered.

I. Introduction

A theoretical treatment of diffusion in liquid crystals is needed to explain recent experimental results. Doane⁽¹⁾ has measured the anisotropy of diffusion of tetramethylsilane (TMS) in 4-methoxybenzylidene-4-*n*-butylaniline (MBBA) in the nematic phase utilizing the proton spin-echo technique. Yun and Fredrickson⁽²⁾ have measured the anisotropy of self-diffusion in pure *p*-azoxyanisole (PAA) in the nematic phase. Blinc and Dimic⁽³⁾ and Janik *et al.*⁽⁴⁾ have attributed the broadening of the quasielastic peak in slow neutron scattering experiments on PAA to self-diffusion. Blinc *et al.*[5] also measured the self-diffusion rate in PAA using the spin-echo technique and Pintar *et al.*⁽⁶⁾ related T_1 measurements in NMR

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studies on PAA to the diffusivity. Early work on the anisotropy of the diffusivity in liquid crystal mixtures by Svedberg(7) in a magnetic field indicated that $D^{\parallel} > D > D^{\perp}$ where $D^{\parallel}$ and $D^{\perp}$ are the diffusivities parallel and perpendicular to the field, respectively, and D is that with no field.

The purpose of the work reported here is to adapt contemporary liquid and solid-state diffusion theory to liquid crystals and to relate the theoretical developments to experimental observations. In liquid diffusion theory, which is generally more applicable to liquid crystals than solid-state theory, the work of Kirkwood,(8) Martin and Yip(9) and Rice(10) is utilized in particular. Some solid-state theory by Vineyard,(11) Franklin(12–14) and Rice(15) is also utilized. The next section, Molecular Mechanisms, deals with the elementary processes involved, in a physical sense, in liquid crystal diffusion. In the section, Modified Kirkwood Theory, the diffusivity is developed in tensor form, using an anisotropic viscosity, and related to the detailed molecular structure of PAA and MBBA. In Sec. IV, Rotational Diffusion, a value for D_r is obtained for PAA using the modified Kirkwood theory and the basic concepts of rotational diffusivity are developed for liquid crystals. In the last section, Scattering, Correlation Functions, etc. a number of ideas are discussed briefly.

II. Molecular Mechanisms

Because of the wide diversity of molecular arrangements which are either known or postulated in liquid crystal mesophases at different temperatures, a wide range of experimental observations and theories is expected for diffusion. For example, diffusion in the highly ordered smectics is expected to have many similarities to solids, a high degree of anisotropy is expected in most cases, intramolecular rotations could have a significant effect on molecular translational and rotational diffusion and a coupling between translational and rotational diffusion may be important.

The motion of an atom or ion in a molecule in a many-body system of molecules in the liquid crystalline state can be described in terms of motions of segments of the molecule with respect to its c.m. and of the c.m. itself. In the rigid molecule approximation the shape and size of molecular segments, but not their relative motion, affects the flow of the surrounding medium around the diffusing molecule. If the rigid molecule is not assumed, the bending and rotation of segments will affect both the rotational and translational diffusion of the molecule as a whole. Since most liquid crystal molecules are rather rigid and short, compared to macromolecules like most polymers, the rigid rod assumption can be made for initial calculations without large error. This assumption is made here.

The mechanisms which can be postulated for diffusion in liquid crystals include many that are familiar in solids and liquids. For translational diffusion, the following are possibilities: crowdion type,(16) activated volume,(17) activated diffusing molecule (" hot " molecule),(18) axial rotation of molecular clusters formed by localized fluctuations, etc. They are not mutually exclusive and, even though one may have the lowest activation energy, ΔE, others with higher ΔE may be operative depending on the magnitude of the pre-exponential part as well as ΔE. These processes have been well described in the literature(16–18) but a word should be said about the last mechanism listed. This is the ring rotation mechanism(16) and may involve different numbers of molecules in the ring. The activation volume and energy are low for this process but the probability for cooperative motion decreases sharply with increasing numbers of molecules. An additional possibility for this mechanism, which is unique for liquid crystal systems, is that translational motion parallel to the localized director could occur simultaneously with cluster rotation.

The exact mechanism for a given compound and mesophase is difficult to predict theoretically or to determine experimentally. Computer calculations for the ring rotation mechanism have been attempted(19) but realistic calculations will require long times on a computer with a large memory. It seems impossible, at the present time, to perform a realistic computer calculation like that done by Rahman(20) for argon and include the additional variables of angular orientation and velocity, which are needed for liquid crystals, to calculate the diffusivity for various mechanisms. Experimentally, it may be possible to measure the activated volume(17) by an NMR technique utilizing the pressure dependence of the diffusivity and to infer the mechanism from the results.

III. Modified Kirkwood Theory

In the macroscopic, as well as the microscopic, sense the diffusivity is normally described by a second rank contravariant tensor D^{ij} which relates the components of the flux J^i to those of the gradient, in generalized coordinates, of the electrochemical potential $\partial\mu/\partial q^j$.

$$J^i = -D^{ij}\,\partial\mu/\partial q^j \tag{1}$$

Nonlinear effects can be included as higher order tensors such as D^{ijk} in a phenomenological manner but they can also be included within D^{ij},⁽¹³⁾ which is what will be assumed here. The importance of nonlinear terms in liquid crystal theory⁽²¹⁾ may necessitate their inclusion in diffusion theory but the linear assumption will be adopted here as a first approximation.

In order to discuss self- as well as impurity diffusion, a space-time correlation function $[G(q_r, t)]$ can be defined in generalized coordinates q_r which are a function of position r. This function is separable into " self " and " distinct " parts⁽²²⁾ G_s and G_d and the function G_s will be called the self-diffusion correlation function⁽²³⁾ since it gives the probability of finding a molecule with coordinate q at position r and time t given q at the origin at time $t = 0$. Fick's second law can then be written

$$\partial G_s/\partial t = (\partial/\partial q^i)\,D^{ij}\,(\partial G_s/\partial q^j) \tag{2}$$

where D^{ij} is dependent on q^i at position r in the general case. Both translational and rotational self-diffusion are amenable to treatment using G_s. In addition, conditional probability correlation functions could be utilized.

The anisotropy of a mesophase is determined by its point and space symmetry group. For aligned nematic and smectic A and B compounds the $C_{\infty v}$ symmetry leaves two nonvanishing independent components of D^{ij} in the principal axis representation. If x is chosen parallel to the director, then the matrix elements of the diffusivity are given by

$$D = \begin{pmatrix} D^{\parallel} & 0 & 0 \\ 0 & D^{\perp} & 0 \\ 0 & 0 & D^{\perp} \end{pmatrix} \tag{3}$$

where $D^{\parallel}$ and $D^{\perp}$ are the diffusivities parallel and perpendicular to the director, respectively. In cholesterics, if z is chosen as the optic axis, $D = D(z)$ and

$$D(z) = \begin{pmatrix} D_x & 0 & 0 \\ 0 & D_y & 0 \\ 0 & 0 & D_z \end{pmatrix}_z . \tag{4}$$

In the smectic C mesophase the situation is complicated but rotation to principal axes can always be done so that (4) would apply in this case also.

The phenomenological theory of diffusion in liquid crystals in terms of the parameters ζ, the friction constant, and η, the viscosity, is best developed in terms of the Kirkwood theory(8) of the diffusion of macromolecules in an isotropic solvent. This is accomplished by adapting the theory to self-diffusion and to anisotropic media utilizing an anisotropic viscosity in place of the solvent viscosity η_0 in Kirkwood's theory. In addition, the assumption made by Kirkwood that the molecule is comprised of identical chain elements is not made here since, in fact, most liquid crystal molecules have chain elements which differ considerably from each other. Also, the effects of order in the aligned state are found to affect the theory.

In liquids and liquid crystals the diffusivity is related to the friction tensor following the Einstein theory(24) by

$$D^{ij} = kT(\zeta^{-1})^{ij} \tag{5}$$

where $\zeta = \zeta_0 \exp(\Delta G/kT)$ for an activated process. Since the friction constant can be found from data taken at the temperature of diffusion, the activation energy need not be considered here. From Kirkwood, we have

$$D^{ij} = kT(g^{ij}/\zeta + T^{ij}) \tag{6}$$

where g^{ij} is the metric tensor in molecular chain space, ζ is the scalar friction constant and T^{ij} is the Oseen hydrodynamic interaction tensor which accounts for the effects of other segments of a molecule on the diffusion of a particular segment.

The changes which are introduced into Kirkwood's theory in order to make the theory more realistic for liquid crystals can best be seen in the Oseen tensor which is given by

$$T_{ls}^{ij} = \sum_{\sigma,\nu} \frac{g^{i\sigma} g^{j\nu}}{8\pi\eta R_{ls}} \left[\frac{\partial \mathbf{R}_l}{\partial q^\sigma} \cdot \frac{\partial \mathbf{R}_s}{\partial q^\nu} + \frac{[\mathbf{R}_{ls} \cdot (\partial \mathbf{R}_l/\partial q^i)][\mathbf{R}_{ls} \cdot (\partial \mathbf{R}_s/\partial q^j)]}{R_{ls}^2} \right] \tag{7}$$

where $\mathbf{R}_l$ is the position vector of segment l with respect to an external reference frame, $\mathbf{R}_{ls}$ is the difference between the position vectors for segments l and s, and q^n is the nth generalized coordinate of molecular chain space. Since the molecules of interest here have an odd number of segments the segments will be numbered from $-n$ to $+n$ and are connected by $2n$ bonds of bond vector $\mathbf{b}_l$. The chain space is a subspace of the $6n+3$ dimensional configuration space and its dimensionality will be governed by the constraints put on the system. We consider here a system of aligned molecules in which each molecule is constrained to be a rigid rod but in which, in contrast to Kirkwood, the molecular segments may vary in length. In this case, the covariant metric tensor for space coordinates q^n is given by

$$g_{ij} = \sum_{l=-n}^{+n} \frac{\partial \mathbf{R}^l}{\partial q^i} \cdot \frac{\partial \mathbf{R}^l}{\partial q^j} = \sum_{l=-n}^{+n} \frac{1}{b^2} b_{l_i} b_{l_j} \hat{e}_i^l \cdot \hat{e}_j^l \tag{8}$$

where b is taken here as the average of the two minor axes of the molecule. Note should be taken here that the unit of measure adopted here is b, not the length of an average chain segment. Also, it should be noted that in an aligned system the projection of $\mathbf{R}$ onto perpendicular coordinate axes is small for strong alignment.

Detailed molecular models of both PAA and MBBA have been made and the reader is referred to another article$^{(25)}$ for the calculations. In this model, $g_{ij} = \mu\, \delta_{ij}$ where $\mu = 2.95$ for PAA and 3.16 for MBBA. The diffusivities both parallel and perpendicular to the axis of the director were obtained and are given by

$$D^{\parallel} = kT\left(\frac{1}{\mu\zeta} + \frac{\lambda}{4\pi\mu^2 b^2 \eta^{\parallel}}\right) \tag{9}$$

$$D^{\perp} = kT\left(\frac{1}{\mu\zeta} + \frac{\lambda}{8\pi\mu^2 b^2 \eta^{\perp}}\right) \tag{10}$$

respectively where

$$\lambda = \sum_{l,s=-n}^{+n} b_l b_s / R_{ls} \quad (l \neq s) \tag{11}$$

The anisotropy of D can be shown quantitatively by either the difference equation $D^{\parallel} - D^{\perp}$ or the ratio $D^{\parallel}/D^{\perp}$. The diffusivities given by (9) and (10) were calculated for PAA using the viscosity data given by Fisher and Fredrickson.$^{(26)}$ Since the friction constant, in addition to the diffusivities, is unknown there are three unknowns and only two equations. Therefore, the self-diffusion constant for unoriented PAA obtained by Yun and Fredrickson^(2) ($D_0 = 3.5 \times 10^{-6}$ cm²/s) was used to obtain ζ. This was done by setting (1/3) Trace $D^{ij} = D_0$ and using $\eta^{\parallel}$ and $\eta^{\perp}$ in this equation to obtain a value of the friction constant $\zeta = 6.7 \times 10^{-9}$ gm/s. Using this value of ζ, obtained at 125 °C, the following values of the diffusivity were obtained for self-diffusion in PAA at the same temperature

$$D^{\parallel} = 4.25 \times 10^{-6} \text{ cm}^2/\text{s} \tag{12}$$

$$D^{\perp} = 2.87 \times 10^{-6} \text{ cm}^2/\text{s} \tag{13}$$

which gives a ratio of $D^{\parallel}/D^{\perp} = 1.48$ and a difference of $D^{\parallel} - D^{\perp} = 1.38 \times 10^{-6}$ cm²/s. The experimental values of Yun and Fredrickson^(2) are $D^{\parallel} = 4.0 \times 10^{-6}$ and $D^{\perp} = 3.2 \times 10^{-6}$ cm²/s at 125 °C which give a ratio of $D^{\parallel}/D^{\perp} = 1.25$ and a difference of $D^{\parallel} - D^{\perp} = 0.80 \times 10^{-6}$ cm²/s.

The agreement between theory and experiment is particularly pleasing in view of the fact that the unmodified Kirkwood theory gives values quite different from the above. In that case, $D^{\parallel} = 1.65 \times 10^{-6}$ and $D^{\perp} = 5.5 \times 10^{-7}$ cm²/s were obtained giving a ratio of $D^{\parallel}/D^{\perp} = 3.0$. Another pleasing feature is that $D^{\parallel}/D^{\perp} = 1.48$ in the modified Kirkwood theory whereas the inverse ratio of viscosities in PAA at 395 °K is much larger^(26) and is given by $\eta^{\perp}/\eta^{\parallel} = 3.8$. The diffusivity is inversely proportional to the viscosity but, as Eqs. (9) and (10) show, the viscosity appears in the second term whose magnitude with respect to the first term depends on the molecular geometry and the friction constant. Consequently, the detailed molecular geometry affects the results quite significantly.

A calculation similar to that outlined above was made for MBBA. In this case, the diffusivities measured by Doane^(1) for a concentration of about 5% TMS in MBBA were used to estimate the properties of MBBA. Since this is a rather concentrated solution, it probably does not correspond to the diffusivity in pure MBBA. However, a calculation was made anyway in order to relate the interesting anisotropy ratios of the diffusivity in MBBA and PAA to those of the viscosity in these compounds. Since ζ in the Kirkwood theory is a scalar, the molecular geometry is embodied primarily in the metric tensor g_{ij}. Therefore, ζ calculated for PAA was utilized for MBBA—a choice which may introduce a small error. The difference between the molecules which affects the diffusivity calculation is one of the tails which is —C_4H_9 for MBBA and —OCH_3 for PAA which have calculated lengths of 4.22 Å and 2.78 Å respectively. For a diffusing molecule, this is apparently the only major difference between the two compounds. The MBBA/PAA mass ratio is only 1.035 and should not affect the diffusivity significantly and the differences in the double bond region at the centers of the molecules are not deemed significant in diffusion.

Doane's(1) measured values of the diffusivity of TMS in MBBA are $D^{\parallel} = 3.4 \times 10^{-5}$ and $D^{\perp} = 0.9 \times 10^{-5}$ cm²/s. Cohen and Turnbull(17) have shown that the diffusion rate of a small concentration of impurity should equal that of the solvent when the size of the impurity is $\leqslant$ that of the solvent molecule. However, since a high concentration of TMS was used (5%), a detailed calculation of the mixture of molecules would have to be made to have a realistic relationship to the experiment. However, since $D \sim m^{-1/2}$, the relationship between the diffusivities of pure MBBA and TMS in MBBA can be approximated by

$$D_{\mathrm{MBBA}}/D_{\mathrm{TMS}} = (m_{\mathrm{TMS}}/m_{\mathrm{MBBA}})^{1/2} \tag{14}$$

which gives a value of 0.607. Making this approximation, we estimate the diffusivities of pure MBBA to be $D^{\parallel} = 2.06 \times 10^{-5}$ and $D^{\perp} = 0.55 \times 10^{-5}$ cm²/s. With these approximations the viscosities were calculated using Eqs. (8) and (9) and found to be $\eta^{\perp} = 4.14 \times 10^{-3}$ and $\eta^{\parallel} = 1.50 \times 10^{-3}$ poise which gives the ratio $\eta^{\perp}/\eta^{\parallel} = 2.76$. These viscosities are too low since they are not even as high as water which is 10^{-2} poise. If the diffusivities and the friction constant in pure MBBA were lower than those estimated here, the values of the viscosities would be increased. An important thing to note here is that the ratio of diffusivities in MBBA is 3.78 whereas that for PAA is only 1.25. The observed viscosity ratio for PAA is $\eta^{\perp}/\eta^{\parallel} = 3.83$ whereas that calculated for MBBA is 2.76. Therefore, it is possible with the modified Kirkwood theory, to obtain significantly different ratios for $D^{\parallel}/D^{\perp}$ and $\eta^{\perp}/\eta^{\parallel}$ in the same compound (PAA in this case) whereas small changes in the molecular geometry alter these ratios significantly, as shown for MBBA.

IV. Rotational Diffusion

A rotational velocity distribution function $G(\omega, t;\ \omega_0, O)$ can be defined so that Fick's first and second laws are given by

$$\mathbf{j} = D_r \cdot \nabla_\phi G \tag{15}$$

$$\partial G/\partial t = \nabla_\phi \cdot \mathbf{j} = \nabla_\phi \cdot D_r \cdot \nabla_\phi G \tag{16}$$

where $\mathbf{j}$ is the reorientation flux vector, ϕ_i are the rotation angles, ∇_ϕ is the gradient with respect to these angles and ω is the rotation frequency. In some liquid crystals D_r can depend on location through the dependence of ϕ on spacial coordinates. Without this dependence, (16) becomes

$$\partial G/\partial t = D_r \cdot \nabla_\phi \cdot \nabla_\phi G \tag{17}$$

If the condition given by $\xi_i t/I \gg 1$ is fulfilled, then the rotational diffusivity is given by $D_r^{ij} = kT(\xi^{-1})^{ij}$[27] where ξ is the rotation friction constant. The diffusion equation is then

$$\partial G/\partial t = kT(\xi^{-1})^{ij}(\partial/\partial\phi^i)(\partial G/\partial\phi^j). \tag{18}$$

In the Kirkwood theory, however, D_r is given by (6) and the rotational friction constant is given by ζ/g^{ij}. In addition, (6) includes the Oseen hydrodynamic tensor. For rotation of a cylindrical rod the components of the metric tensor are diagonal and are given by $g_{11} = 1$, $g_{22} = r^2$ and $g_{33} = r^2 \sin^2$ for the covariant tensor and the inverse of these for the contravariant case. For a molecule comprised of $2n+1$ non-identical segments, the covariant components are given by

$$\begin{aligned} g_{11} &= 1 \\ g_{22} &= \sum_{l=-n}^{+n} \xi_l^2 \\ g_{33} &= \sin^2\theta \sum_{l=-n}^{+n} \xi_l^2 \end{aligned} \tag{19}$$

where

$$\xi_l = 1/2(b_0 + b_l) \sum_{1}^{|l|-1} b_n. \tag{20}$$

Using this form of the metric tensor it can be shown that

$$D^{\theta\theta} = \frac{kT}{\zeta\epsilon}\left(1 + \frac{\zeta\Omega}{8\pi\eta^{\perp}\epsilon}\right) \tag{21}$$

where

$$\epsilon = \sum_{l=-n}^{+n} \xi_l^2 \tag{22a}$$

$$\Omega = \sum_{s \neq l = -n}^{+n} \frac{\xi_l \xi_s}{|\xi_l - \xi_s|} . \tag{22b}$$

Utilizing values given above for PAA at 395 °K, the value calculated for the rotational diffusivity from (20) is $D^{\theta\theta} = 6.95 \times 10^8$ sec^{-1}. The value of $D^{\phi\phi}$ is given by $D^{\phi\phi} = D^{\theta\theta}/\sin^2\theta$ where an ensemble average should be used for $\langle \sin^2\theta \rangle$ which can be related to the order parameter.

V. Scattering, Correlation Functions, etc.

In this section a variety of topics are discussed briefly but reflect, in some cases, extensive calculations done elsewhere.

Since some of the smectics are closer to solids in their physical properties than other liquid crystals, it will be interesting to see if some of the attributes of solid-state diffusion theory apply to these systems. Usually the theory of solid-state diffusion is couched in terms of the difference in free energy between equilibrium states at the bottom and top of a col. The diffusivity is written

$$D = \alpha l^2 \nu \, e^{(S_f + S_m)/k} \, e^{-(H_f + H_m)/kT} \tag{23}$$

where α is a geometrical factor, l is the jump distance, ν is a vibration frequency, and S_f, S_m and H_f, H_m are the entropies and enthalpies of formation and motion, respectively, of a defect. In compounds which form liquid crystals, the diffusion mechanism in their solid state is probably similar to that of other organics of similar size and could, therefore, proceed by a molecular defect mechanism such as the vacancy mechanism. In that case, a separate free energy of formation and probability of occurrence of the defect can be written as done in (23). In some smectics the theory could probably be formulated in this manner. If the mechanism does not involve well established defects the free energy can be written as a difference between that at the saddle-point and the equilibrium configuration with a finite velocity at the saddle-point in the migration direction.(12,15,17) Cohen and Turnbull's theory(17) can be written in many-body theory as done by Franklin(12) for solids in which the displacements in a many-body system required in order for diffusion to occur can be written directly in the potential. The activation volume then becomes a sum of critical displacements of all the molecules involved in the diffusion event. When this is done in the harmonic approximation the activation energy over kT becomes

$$\frac{\Delta E}{kT} \cong \sum_{\alpha\beta}^{3} \sum_{ij}^{N} \frac{[u_\alpha^c(i)]^2}{\langle u_\alpha(i) u_\beta(j) \rangle} \tag{24}$$

where $u_\alpha^c(i)$ and $u_\alpha(i)$ are the critical and thermal displacements, respectively, of the ith molecule in the α direction.

Another thing to note about Eq. (23) is that $D \sim l^2$. If the jump distance in liquid crystals is equal to a molecular dimension such as, for example, the length in $D^{\parallel}$ and the width in $D^{\perp}$ in PAA, then the ratio of the magnitude of the diffusivities is given by $D^{\parallel}/D^{\perp} = 17.4^2/5.1^2 = 11.7$ where the average of the two minor axes is used for the width. This ratio is much higher than 1.25, which is observed experimentally,(2) which indicates that the vacancy type of mechanism is not operative for PAA unless there is a significant difference in the free energies parallel and perpendicular to the axis of the director.

The diffusivity, both translational and rotational, can affect the scattering of thermal neutrons in quasielastic scattering from liquid crystals.(3,4) The broadening of X-ray peaks and of Rayleigh peaks in light scattering is also affected by diffusion. The very unusual behavior found by Blinc and Dimic(3) in PAA that the quasielastic scattering of slow neutrons was independent of temperature in the nematic region was studied here. If the scattering was due to translational or rotational diffusion in the usual sense, some temperature dependence almost seems mandatory. This can be shown in various ways and the detailed temperature deviation from inverse linear dependence in the exponential has been worked out for solids in the high temperature anharmonic case and the low temperature quantum-harmonic case.(28) Rather than show these theories here, which are rather cumbersome, a simple phenomenological theory developed by Mehrer and Seeger(29) for self-diffusion in metals will be outlined and applied to liquid crystals. From (5), in the case of an activated process, we let $\Delta G = H(T) - S(T)T$ in which both the enthalpy and entropy are T dependent. If we let

$$H(T) = H(T_0) + \alpha k(T - T_0), \tag{25}$$

then

$$S(T) = S(T_0) + \alpha k \ln T/T_0, \tag{26}$$

where α is a unitless parameter. If a region or point of temperature independence exists, then $\partial D/\partial T = 0$ there and the temperature at which this occurs (T_c) determines a value of α which is given by

$$\alpha = \frac{H(T_0) + T_c}{T_c - T_0}. \tag{27}$$

These values of α, when used in the diffusivity, which is given by

$$D = \frac{kT}{\zeta_c}\left(\frac{T}{T_c}\right)^{\alpha} e^{S_c/k - [Q/kT + \alpha(T - T_c)/T]}, \tag{28}$$

result in rather large differences in D with small temperature change. For example, if PAA is considered and the activation energy chosen to be in the range of 0.1–0.3 eV, then a range of ratios $D(395\,°\mathrm{K})/D(375\,°\mathrm{K})$ of 1.3–5.1 is obtained. Consequently, if the activation energy is in the usual range for either translational or rotational diffusion in liquids of small molecules, the temperature variation should be measurable in the nematic range. It should also be noted that it is highly unlikely that the temperature dependence of H and S should give a minimum in $D(T)$ in the particular temperature range observed in PAA. The upshot of this analysis is that the observations of no temperature dependence of the neutron scattering cross section in PAA in the nematic range$^{(3)}$ probably indicates a non-activated process or a very small temperature dependence which was experimentally unobservable.

An interesting result of the analysis of both translational and rotational diffusion in PAA is that the distance a molecule diffuses during a rotational lifetime can be calculated. This is done by setting the lifetime equal to D_r^{-1} so that, for PAA, we get

$$x^{\parallel} = (D_{\mathrm{tr}}^{\parallel}/D_r)^{\frac{1}{2}} = 7.82\,\text{Å} \tag{29}$$

$$x^{\perp} = (D_{\mathrm{tr}}^{\perp}/D_r)^{\frac{1}{2}} = 6.43\,\text{Å} \tag{30}$$

where D_{tr} denotes translational diffusion. This is an interesting result for the perpendicular case, since it is close to the average of the minor axes, and the consequences should be investigated more thoroughly.

Another result interesting in liquid crystal theory is obtained from Eq. (24) if the usual transformation for the displacement u is adopted. In this case, $u \sim \omega^{-\frac{1}{2}}$ so that $\Delta E/kT \sim \omega^{-1}$. Therefore, if the low frequency dissipative modes found by the Orsaay group(31) are stimulated in large numbers, such as in the scattering of laser light, an effect on diffusion might be observable.

A prediction made by the Kirkwood and the modified Kirkwood diffusion theory is the dependence of D on molecular length for a series of similar compounds. In the Kirkwood theory the first term in Eqs. (9) and (10) is inversely proportional to n, the number of chain segments while the second term is a slowly increasing function of n. Therefore, if the first term is sufficiently large with respect to the second, D decreases with n. The exact dependence, for a series of similar compounds, on the molecular geometry can be approximated by using the modified Kirkwood theory.

The jump time of an actual diffusion event, that is, the time of an actual translational process, can be calculated for a particular compound if something is known about the average potential. For example, Franklin and Graddick(14) developed an equation for the jump time in metals using a Morse potential (see Eq. (37) of Ref. 14) which could be evaluated numerically. In liquid crystals, the hydrogen–hydrogen non-bonded potential could be utilized and an approximation for the jump time obtained. The energy exchange between the migrating molecule and localized or collective excitations is a rather complicated process but through the utilization of Hamilton–Jacobi theory in an effective three-body simulation of the condensed state, it is possible to calculate the exchange and the resonances involved.(14) The energy exchange during a migration event affects the observed mass dependence, as in polaron theory, so that the " dressed " mass of the particle will be a bit larger than the molecular mass.

The relationship of the diffusivity to the dispersion of frequencies and to the spectral distribution function offers an alternative, in ways of attacking the problem, to Kirkwood's method. If this is done, following the work of Martin and Yip,(9) an equation for the diffusivity is obtained which is given by

$$D = \frac{kT}{m\tau(\langle\omega^2\rangle - \omega_0^2)} \tag{31}$$

where τ is a relaxation time, $\langle\omega^2\rangle$ is an ensemble average over the frequency distribution and ω_0 is the frequency for the molecule as a harmonic oscillator in a potential well. If ω_0 is taken as zero, which is often done for liquids,⁽⁹⁾ then D can be estimated for PAA using a relaxation time measured by Blinc and Dimic⁽³⁾ of $\tau = 2.5 \times 10^{-12}$ and an ensemble frequency average adapted from computer work done by Rahman⁽²⁰⁾ for argon. Since $\omega \sim \mathrm{m}^{-\frac{1}{2}}$ then $\langle\omega^2\rangle \sim \mathrm{m}^{-1}$ and if we assume that the ratio of the average frequency squared is valid for argon and PAA, then we get $\langle\omega^2\rangle(\mathrm{PAA})/\langle\omega^2\rangle(\mathrm{A}) = m(\mathrm{A})/m(\mathrm{PAA})$ which gives a value of $\langle\omega^2\rangle(\mathrm{PAA}) = 7.3 \times 10^{24}$. The value of D obtained from (31) at a temperature of 395 °K is then 7.0×10^{-6} cm²/s which is not widely different from that obtained from Kirkwood's approach. The approximations in this procedure limit its reliability but as more data becomes available a closer relationship can be established between D, τ, $\langle\omega^2\rangle$ and ω_0^2.

Another formalism which was considered and which could, perhaps, be useful for liquid crystals involves the relationship between the diffusivity and the dissipative portion of the stress tensor, σ'_{ij}. The six Ericksen-Leslie⁽³¹⁾ viscosity coefficients have been related to σ' and could be related to the diffusivity. However, without a knowledge of all the viscosity coefficients, the relationship would not be as useful as the modified Kirkwood technique for the actual evaluation of D for a given compound.

NOTE

Since the completion of this article the order parameter and temperature dependence were introduced into the modified Kirkwood theory for PAA. The results are reported elsewhere⁽²⁵⁾ but, in brief, the temperature dependence was so small that Blinc and Dimic⁽³⁾ probably could not observe it and the order parameter introduced curvatures in $D^{\parallel}$ and $D^{\perp}$ near the isotropic transition. Very close correspondence with the temperature dependent experimental results of Yun and Fredrickson⁽²⁾ was obtained.

REFERENCES

1. Doane, J. W., *III International Liquid Crystal Conference* (1970).
2. Yun, C. and Fredrickson, A. G., to be published.
3. Blinc, R. and Dimic, V., *Phys. Letters* **31A**, 531 (1970).
4. Janik, J. A., Janik, J. M., Otnes, K. and Riste, T., *III International Liquid Crystal Conference* (1970).
5. Blinc, R., Hogenboom, D. L., O'Reilly, D. E. and Peterson, E. M., *Phys. Rev. Letters* **23**, 969 (1969).
6. Dong, R. Y., Forbes, W. F. and Pintar, M. M., to be published.
7. Svedberg, V., *Kolloid Zeitschrift* **22**, 68 (1918).
8. Kirkwood, J. G., " Macromolecules " edited by P. L. Auer, Gordon and Breach, New York, 1967.
9. Martin, P. C. and Yip, S., *Phys. Rev.* **170**, 151 (1968).
10. Rice, S. A., in " Liquids: Structure, Properties, Solid Interactions," edited by T. J. Hughel, Elsevier Publ. Co., Amsterdam, 1965, p. 51.
11. Vineyard, G. H., *J. Phys. Chem. Solids* **3**, 121 (1957).
12. Franklin, W., *J. Phys. Chem. Solids* **28**, 829 (1967).
13. Franklin, W., *Phys. Rev.* **180**, 682 (1969).
14. Franklin, W. and Graddick, W., *Phys. Rev.* **82**, 2906 (1970).
15. Rice, S. A., *Phys. Rev.* **112**, 804 (1958).
16. Lazarus, D., *Solid State Phys.* **10**, 222 (1960).
17. Cohen, M. H. and Turnbull, D., *J. Chem. Phys.* **31**, 1164 (1959).
18. Glasstone, S., Laidler, K. J. and Eyring, H., " The Theory of Rate Processes " (McGraw-Hill Book Co., New York) 1941.
19. Richards, B. and Franklin, W. M., unpublished results.
20. Rahman, A., *Phys. Rev.* **136**, A405 (1965).
21. de Gennes, P. G., *III International Liquid Crystal Conference* (1970).
22. Van Hove, L., *Phys. Rev.* **95**, 249 (1954).
23. Vineyard, G. H., *Phys. Rev.* **110**, 999 (1958).
24. Einstein, A., " Brownian Movement " (Dover Publications, New York) 1956.
25. Franklin, W. to be published.
26. Fisher, J. and Fredrickson, A. G., *Mol. Cryst. and Liq. Cryst.* **8**, 267 (1969).
27. Steel, W. A., *J. Chem. Phys.* **38**, 2404 (1963).
28. Franklin, W. M., *Bull. Am. Phys. Soc.* **13**, 1377 (1968).
29. Seeger, A. and Mehrer, H., in " Vacancies and Interstitials in Metals " (North-Holland, Amsterdam) 1969.
30. Groupe d'Etude des Cristaux Liquides (Orsay), *J. Chem. Phys.* **51**, 816 (1969).
31. Leslie, F. M., *Quart. J. Mech. Appl. Math.* **19**, 357 (1966).