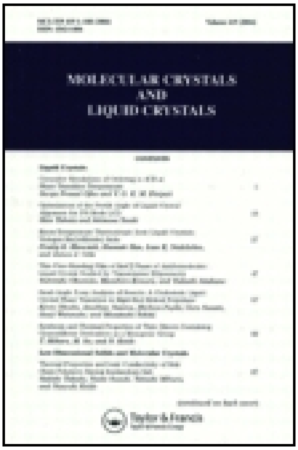

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Translational Self-Diffusion in the Smectic A Phase

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Translational Self-Diffusion in the Smectic A Phase†

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The translational self-diffusion tensor of smetic A liquid crystals is obtained in the hydrodynamic limit of the two fluid model. The diagonalized matrix elements are calculated by utilizing Rice and Kirkwood's intermolecular correlation equation for the friction constant and Einstein's relation for diffusivity. McMillan's potential for the smectic A phase is used in calculations. The anaharmonic effects are taken into consideration in the preferred direction of molecular alignment. The results are qualitatively compared with a spin echo measurement reported by Krüger *et al.*

I INTRODUCTION

The various and distinct structures of liquid crystals, or ordered fluids, certainly lead one to suspect that molecular diffusion might have unusual properties reflecting the high anisotropy. Knowledge of the diffusion tensor in the liquid crystalline phases may therefore not only give some information as to the liquid crystal structures, but also some insight into other properties of physical interest and the molecular dynamics of liquid crystalline systems.

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Since liquid crystals are states intermediate between those of a solid crystal and a liquid, one would expect to adapt well-established theories for diffusion in both solids and liquids. Kirkwood, Buff, and Green,[1] on the basis of a dimensional analysis suggested the relation for the friction constant

$$\xi^2 = \frac{Nm}{3v}\int \nabla^2 V_{12}(r) g^{(2)}(r) d^3 r \tag{1}$$

with $g^{(2)}(r)$ the equilibrium pair correlation function, and $V_{12}(r)$ the pair interaction potential. Rice and Kirkwood[2] derived Eq. (1) by assuming that diffusion in a dense fluid proceeds by a series of displacements, each small compared to the interatomic spacing. Collins and Raffel[3] also derived Eq. (1) by a totally different method which utilizes the assumption that the initial curvature of a decay trajectory, say the momentum of a "hot" molecule, is equal and opposite to the curvature at a later time. Rice[4] again obtained the same result as Eq. (1) with only a factor $2/\pi$ difference by a precise determination of the fractional coefficient in terms of the intermolecular forces. His approach explored briefly the dynamical behavior of the molecules and characterized the irreversibility of the motion in a suitable manner so that it is the nature of the intermolecular correlations which defines the approach to equilibrium.

Based on these works, we believe that the utilization of Eq. (1) will give us a simple direct approach to the calculation of the diffusion tensor in the highly ordered smectic A phase.

II THEORY

In a smectic A liquid crystal, the centers of mass of the molecules are randomly placed in parallel equidistant planes. The long axes of the molecules are aligned along a preferred direction nearly parallel to the normal of the plane.

Due to the layer structure of the smectic A phase, the molecules behave more or less as they would in a solid phase along the preferred direction of molecular alignment. We will treat this direction as a solid phase. Along the planes, we will treat it as a liquid.

McMillan[5-6] suggests a one-body potential for the smectic A phase

$$V_1(z, \cos\theta) = -V_0\left[s\left(\tfrac{3}{2}\cos^2\theta - \tfrac{1}{2}\right) + \Lambda\lambda\mu\cos\left(\frac{2\pi z}{d}\right) + \Lambda\sigma\cos\left(\frac{2\pi z}{d}\right)\left(\tfrac{3}{2}\cos^2\theta - \tfrac{1}{2}\right)\right] \tag{2}$$

in which θ is the angle between the long axis of the molecules and the preferred direction of molecular alignment, z-axis; d is the interplanar spacing; s is the orientational order parameter; μ is the positional order parameter; σ is a mixed order parameter between the orientation and the position of the molecules; and V_0, Λ and λ are potential parameters. They are fixed by requiring the model to fit the measured smectic-cholesteric and cholesteric-isotropic transition temperatures and the smectic-cholesteric transition entropy. These order parameters are defined by

$$s = \langle \tfrac{3}{2}\cos^2\theta - \tfrac{1}{2} \rangle$$

$$\mu = \left\langle \cos\left(\frac{2\pi z}{d}\right) \right\rangle$$

$$\sigma = \left\langle \cos\left(\frac{2\pi z}{d}\right)(\tfrac{3}{2}\cos^2\theta - \tfrac{1}{2}) \right\rangle \tag{3}$$

and the potential parameter, Λ, is defined by

$$\Lambda = 2\exp\left(-\frac{\pi r_0}{d}\right)^2 \tag{4}$$

where r_0 is of the order of the length of the rigid section of the molecule.

From the time expansion of the momentum autocorrelation function,[4, 7] it can be shown straight forwardly that the dynamical quantity, $\langle \dot{\mathbf{p}}^2 \rangle$ of the observed diffusion molecule can be expressed as

$$\langle \dot{\mathbf{p}}^2 \rangle = k_B T \langle \nabla^2 V_1 \rangle = N k_B T \langle \nabla^2 V_{12} \rangle \tag{5}$$

where the thermal averages are taken in the corresponding one-body laboratory system and two-body relative system. Substituting Eq. (2) into Eq. (5) yields

$$\langle \dot{\mathbf{p}}^2 \rangle = 4\pi^2 \Lambda V_0 k_B T(\lambda\mu^2 + \sigma^2)/d^2 \tag{6}$$

or

$$\langle \nabla^2 V_{12} \rangle = 4\pi^2 \Lambda V_0(\lambda\mu^2 + \sigma^2)/d^2 N \tag{7}$$

Substituting Eq. (7) into Eq. (1) multiplied by the factor $2/\pi$, one finds immediately the apparent, or average, frictional constant of the smectic A liquid crystal

$$\xi = d^{-1}[\tfrac{8}{3}\pi m \Lambda V_0(\lambda\mu^2 + \sigma^2)]^{1/2} \tag{8}$$

From Einstein's relation one obtains, again, immediately the average diffusion coefficient

$$D = k_B T d[\tfrac{8}{3}\pi m \Lambda V_0(\lambda\mu^2 + \sigma^2)]^{-1/2} \tag{9}$$

Now we turn to calculate the anisotropic components of the diffusion tensor $D_\perp$ and $D_\parallel$, perpendicular and parallel to the preferred direction of molecular alignment respectively.

The Hamiltonian of the diffusing molecules in the equilibrium state along the z-axis can be written as

$$H = \frac{p_z^2}{2m} + \phi(z) \tag{10}$$

where $\phi(z)$ is the anharmonic potential with the periodicity of molecular layer separation d and is obtained by taking the ensemble average of $V_1(z, \cos\theta)$ over the orientational space,

$$\begin{aligned} \phi(z) &= \langle V_1(z, \cos\theta)\rangle_\theta \\ &= -V_0\left[\left\{s + \Lambda\sigma\cos\left(\frac{2\pi z}{d}\right)\right\}g(z) + \Lambda\lambda\mu\cos\left(\frac{2\pi z}{d}\right)\right] \end{aligned} \tag{11}$$

where

$$g(z) = \frac{\displaystyle\int(\tfrac{3}{2}\cos^2\theta - \tfrac{1}{2})\exp\left[\frac{V_0}{k_BT}\left\{s + \Lambda\sigma\cos\left(\frac{2\pi z}{d}\right)\right\}(\tfrac{3}{2}\cos^2\theta - \tfrac{1}{2})\right]\sin\theta\,d\theta}{\displaystyle\int\exp\left[\frac{V_0}{k_BT}\left\{s + \Lambda\sigma\cos\left(\frac{2\pi z}{d}\right)\right\}(\tfrac{3}{2}\cos^2\theta - \tfrac{1}{2})\right]\sin\theta\,d\theta}$$

This pre-averaging process of $V_1(z, \cos\theta)$ about θ is for the purpose of later simplification of equations and includes the possible effects due to the rotational motions of the molecules. The equation of motion then is

$$\dot{p}_z = -\frac{\partial H}{\partial z} = -\phi'(z) \tag{13}$$

Thus

$$\langle\dot{p}_z^2\rangle = \frac{\int\phi'^2\exp(-\phi/k_BT)dz}{\int\exp(-\phi/k_BT)dz} \tag{14}$$

Integrating Eq. (14) by parts between the planes once yields

$$\langle\dot{p}_z^2\rangle = k_BT\int\phi''\exp(-\phi/k_BT)dz\Big/\int\exp(-\phi/k_BT)dz \tag{15}$$

To evaluate the integrals involved in Eq. (15), we write

$$\int\phi''\exp(-\phi/k_BT)dz = \int\exp[f(z)]dz \tag{16}$$

where

$$f(z) = \ln\phi'' - \phi/k_BT \tag{17}$$

Since $\phi(z)$ is an even periodic function about z, so is $f(z)$. Suppose that the maximum potential occurs at $z = z_0$, then $\phi'(z_0)$ vanishes. Note that, for a highly anharmonic potential, there exists highly anharmonic effects. Also, there is more than one position for a relative maximum potential. Since only those molecules at or near z_0 are more activated and are therefore most apt to diffuse, we will expand the function $f(z)$ into a power series in $\varepsilon = (z - z_0)$ in the vicinity of z_0. This can be done because both $\phi(z)$ and $f(z)$ are finite and analytical at z_0, i.e., all their derivatives exist at $z = z_0$.

$$f(z) = f(z_0) + \varepsilon f'(z_0) + \frac{\varepsilon^2}{2} f''(z_0) + \cdots$$

$$\cong \ln \phi''(z_0) - \frac{\phi(z_0)}{k_B T} + \frac{\varepsilon^2}{2}\left\{\frac{\phi''''(z_0)}{\phi''(z_0)} - \frac{\phi''(z_0)}{k_B T}\right\} \tag{18}$$

Since the major contribution to the integral of Eq. (16) occurs near the relative maximum of the potential function $\phi(z)$ at $z = z_0$, the Taylor expansion of $f(z)$ will be approximated by keeping only those terms necessary to get a nontrivial result. All the odd derivatives of $f(z)$ vanish at $z = z_0$ due to the facts that $\phi(z_0)$ is a maximum and that all odd derivatives of $\phi(z)$ vanish at $z = z_0$. Substituting Eq. (18) into Eq. (16) yields

$$\int \phi'' \exp\left(-\frac{\phi}{k_B T}\right) dz$$

$$\cong \phi''(z_0) \exp\left[-\frac{\phi(z_0)}{k_B T}\right] \int \exp\left\{-\frac{1}{2}\left[\frac{\phi''(z_0)}{k_B T} - \frac{\phi''''(z_0)}{\phi''(z_0)}\right]\varepsilon^2\right\} d\varepsilon \tag{19}$$

Its integration gives

$$\int \phi'' \exp\left(-\frac{\phi}{k_B T}\right) dz \cong \sqrt{2\pi}\, \phi''(z_0) \exp\left[-\frac{\phi(z_0)}{k_B T}\right]\left[\frac{\phi''(z_0)}{k_B T} - \frac{\phi''''(z_0)}{\phi''(z_0)}\right]^{-1/2} \tag{20}$$

Since the major contribution to the integral in Eq. (19) occurs at $z = z_0$ or $\varepsilon = 0$ and its vicinity, the use of the integration limits from 0 to ∞ is a good approximation. In an exactly analogous manner, we have

$$\int \exp\left(-\frac{\phi}{k_B T}\right) dz \cong \sqrt{2\pi} \exp\left[-\frac{\phi(z_0)}{k_B T}\right]\left[\frac{\phi''(z_0)}{k_B T}\right]^{-1/2} \tag{21}$$

Substituting Eqs. (20) and (21) into Eq. (15) we obtain

$$\langle p_z^2 \rangle = k_B T \phi''(z_0)\left[1 - \phi''''(z_0) k_B T / \phi''^2(z_0)\right]^{-1/2} \tag{22}$$

Using the time expansion of the momentum autocorrelation function, one can easily show that Eqs. (5) and (1) hold true also for their components.

Comparing these two equations gives

$$\xi_\perp = \left[\frac{m}{3\pi k_B T}\langle \dot{p}_\perp^2\rangle\right]^{1/2} \tag{23}$$

$$\xi_\parallel = \left[\frac{2m}{3\pi k_B T}\langle \dot{p}_z^2\rangle\right]^{1/2} \tag{24}$$

Since $\langle \dot{p}_\perp^2\rangle = \langle \dot{\mathbf{p}}^2\rangle - \langle \dot{p}_z^2\rangle$, a substitution of Eqs. (6) and (22) into Eqs. (23) and (24) yields

$$\xi_\perp = \left[\frac{m}{3\pi}\left\{\frac{4\pi^2\Lambda V_0(\lambda\mu^2 + \sigma^2)}{d^2} - \frac{\phi''(z_0)}{[1 - \phi''''(z_0)k_B T\phi''^2(z_0)]^{1/2}}\right\}\right]^{1/2} \tag{25}$$

$$\xi_\parallel = \left[\frac{2m\phi''(z_0)}{3\pi}\right]^{1/2}\left[1 - \frac{\phi''''(z_0)k_B T}{\phi''^2(z_0)}\right]^{-1/4} \tag{26}$$

Again, from Einstein's relation for diffusion, we immediately obtain

$$D_\perp = k_B T\left[\frac{m}{3\pi}\left\{\frac{4\pi^2\Lambda V_0(\lambda\mu^2 + \sigma^2)}{d^2} - \frac{\phi''(z_0)}{[1 - \phi''''(z_0)k_B T\phi''^2(z_0)]^{1/2}}\right\}\right]^{-1/2} \tag{27}$$

$$D_\parallel = k_B T\left[\frac{2m\phi''(z_0)}{3\pi}\right]^{-1/2}\left[1 - \frac{\phi''''(z_0)k_B T}{\phi''^2(z_0)}\right]^{1/4} \tag{28}$$

If one writes Eqs. (27) and (28) into the Arrhenius form, then the activation energies can be found.

III DISCUSSION

The applications of Eq. (1) and Einstein's relation for diffusion imply the truncation of the time expansion of the momentum autocorrelation function. The validity of the approach depends upon the fact that the correlation time of memory of the system is at least one order smaller than the quantity $(2m/\xi)$. The authors[8] have suggested a self-consistent method without such a generalized truncation. This method involves the higher order calculations, which are mathematically more complex in the case of smectic liquid crystals. However, this method is practical and workable, if necessary.

In order to calculate the average diffusion coefficient and the diagonal elements of the diffusion tensor using Eqs. (9), (27), and (28), it is necessary to know the molecular parameters of the McMillan potential. We made a crude estimate of the diffusion coefficients for 4-ethoxy-benzal-4-amino-n-alkyl-α-methylcinnamate. In the calculation we assume that the potential becomes maximum on the mid-plane between the smectic planes. Our estimated results for the $D_\perp$ and $D_\parallel$ are of the orders of 10^{-6} cm^2/sec and 10^{-7} cm^2/sec, respectively; i.e. $D_\perp/D_\parallel \lesssim 10$. Since no experimental work was done on the diffusion coefficients of these smectogenic compounds with known McMillan potentials, it is impossible to test the present theory quantitatively. However, we are able to compare the results of our calculations *qualitatively* with those of a simple spin echo measurement of the anisotropy of the self-diffusion coefficients in smectic A and B type liquid crystals by Krüger *et al.*[9] They found the range of the ratios $D_\perp/D_\parallel$ for *p*-dodecanoyl-benzylidene-*p*′-aminoazobenzene to be from 2.0 to 7.0 for the smectic A phase, depending on the temperature.

We interpret the discrepancy between the present theoretical and experimental results as follows: We are comparing the results for two different compounds. The molecules in the compound used by Krüger's measurement have three benzene rings whereas those used in our theory have two benzene rings. The activation energy for diffusion for the former is greater than that of the latter due to larger induced electric dipole moment. In this type of partially double-bonded aromatic molecule, the π-electrons can travel for a longer distance, almost freely, from one end of the molecule to another. The number of π-electrons also increases in proportion to that of the benzene rings. Therefore, the self-diffusion coefficient $D_\perp$ in the smectic plane for the compound with the molecules having a larger number of benzene rings is smaller than that of the molecules having a smaller number of benzene rings.

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