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Diffusion of Impurities in Smectic A Phases†

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A simple model, based on a hybrid of solid state and liquid theory, is introduced to obtain the impurity diffusion tensor of spherical molecules at low concentration in ordered systems. The anisotropy ratio of the diffusion coefficients $D_\perp$ (perpendicular to the preferred direction of molecular alignment) and $D_\parallel$ (parallel to it), for tetramethylsilane (TMS) dissolved in the smectic A liquid crystal of 4-*n*-butoxybenzylidene-4′-*n*-octylaniline (BBOA) is calculated at the temperature $T = 53°C$. The result $D_\perp/D_\parallel = 8.6$ agrees rather well with the experimental data of Murphy *et al.*

1 INTRODUCTION

Recent measurements of the diffusion coefficient in the nematic, smectic A, and smectic B phases show unusually large anisotropy in their diffusion coefficients.[1–4] A particularly interesting result of these measurements is that the diffusion coefficient along the preferred direction of molecular alignment $D_\parallel$, is larger than perpendicular to it, $D_\perp$, in the nematic phases,[1–3] whereas the opposite seems to be the case[4] in the smectic phases. Of particular interest to us is the experimental work of Murphy *et al.*[4] who measured the diffusion coefficient of the impurity molecule tetramethylsilane (TMS) dissolved in the ordered nematic, smectic A, and smectic B phases of the compound of 4-*n*-butoxy-benzylidene-4′*n*-octylaniline (BBOA).

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Since the difference in the description of the nematic and smectic phases is the periodic ordering in layers of the center-of-masses of the molecules, this periodicity is implicated in reversing the anisotropy ratio from $D_{\parallel}/D_{\perp} > 1$ for the nematic phase to $D_{\parallel}/D_{\perp} < 1$ for the smectic phase. In this paper, a simple model for the impurity diffusion in ordered systems is presented.

In Section II, the model for the impurity molecule and the host liquid crystal molecules in smectic A phases is discussed. Due to the periodic layer structure along the preferred direction of molecular alignment, a longitudinal acoustic phonon mode exists in this direction just as in solids. In Section III, we present a theory to calculate the activation energy and the jump frequency for diffusion in terms of the dilation operator, and a model potential for the impurity molecule which includes anharmonic effects. The effective mass parallel to the preferred direction is now derived from the energy spectrum of the trapped impurity. The effective mass perpendicular to the preferred direction is calculated from the hydrodynamic theory. In Section IV, the anisotropy ratio of the diffusion coefficients, expressed as the inverse ratio of the corresponding effective masses, is compared with the experimental results of Murphy *et al.*[4] for the smectic A phase.

II MODEL

The impurity molecule (TMS) shown in Figure 1 is regarded as a small hard sphere of mass m and radius r. The host molecule, (BBOA, in the experiments of Murphy *et al.*[4]) is treated as consisting of a hard-core (benzene rings) at the center-of-mass with long soft tails (flexible alkyl chains) on both ends (Figure 2). The hard cores of the host molecules are aligned preferentially along the z-direction and located in layers of separation d. As shown in Figure 3, the region between any two layers is filled with soft tails of the molecules, whereas the intralayer part consists of hard cores of the molecules. The host fluid is thus characterized as a two-fluid system.[5] Further, the impurity molecule is assumed to be small compared with the hard core region of the host liquid crystal molecule but larger than each segment of the flexible alkyl chain.

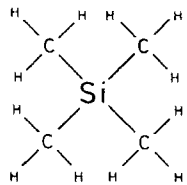

FIGURE 1 Tetrahedral Structure of tetramethylsilane (TMS)

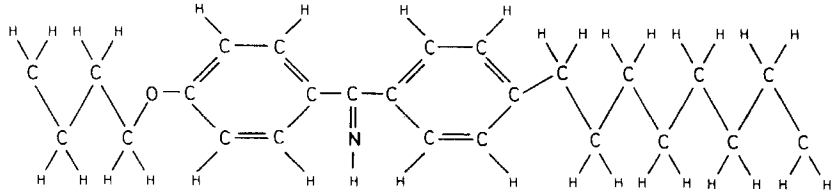

FIGURE 2 Molecular structure of 4-*n*-butoxybenzylidene-4′-*n*-octylaniline (408).

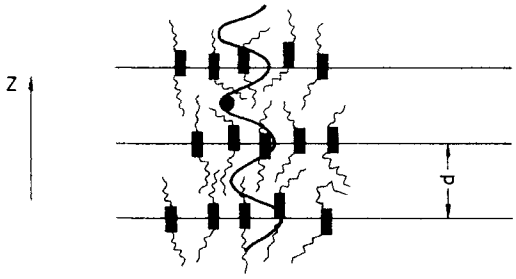

FIGURE 3 Smectic A structure and the trapping states of the impurity. The cosine curve represents the interaction potential between the host molecules and the impurity molecule trapped in the interstitial sites. Here, d is approximately equal to the length of the host molecule.

The process of impurity diffusion along the preferred direction of molecular alignment (longitudinal diffusion) corresponds to diffusion through the hard-core region (the layer) as well as the soft tail region whereas that perpendicular to it (transverse diffusion) implies diffusion across a given soft tail region. The characteristic time constant τ for the longitudinal diffusion process involves the whole molecule, i.e.

$$\tau^{-1} = \tau_h^{-1} + \tau_t^{-1} \tag{1}$$

corresponding to both the hard-core as well as the soft tail regions. For the transverse process on the other hand, only the time constant τ_t corresponding to the soft tail region is required. Due to the layer arrangement of the hard cores of the molecules, the characteristic relaxation time τ_h for the hard-cores is expected to be much greater than τ_t for the soft tail region; thus, one expects $\tau_t^{-1} \gg \tau_h^{-1}$. Eq. (1) can now be written as

$$\tau^{-1} \cong \tau_t^{-1} \tag{2}$$

so that the characteristic relaxation times are essentially the same in longitudinal and transverse impurity diffusion processes.

For the present purpose, only the frequency independent friction coefficients are considered. Using the Einstein relation between the diffusion

coefficient and the friction constant, the anisotropy ratio of the impurity diffusion coefficients can be expressed as

$$\frac{D_{\parallel}}{D_{\perp}} = \frac{\xi_{\perp}}{\xi_{\parallel}} = \frac{m_{\perp}/\tau_t}{m_{\parallel}/\tau}, \tag{3}$$

which, from Eq. (2), becomes

$$\frac{D_{\parallel}}{D_{\perp}} = \frac{m_{\perp}}{m_{\parallel}}, \tag{4}$$

where ξ and m are the friction coefficient and the effective mass of the impurity molecule in the appropriate direction (along the preferred direction and perpendicular to it).

Since the liquid crystal in the smectic A phase has more or less a lattice structure with the periodicity of the layers along the preferred direction of the molecular alignment, it is assumed that there exists a longitudinal acoustic mode (along the preferred direction) just as in solids. However, in the perpendicular direction, the system behaves as a liquid and hence supports no long lived modes (no propagating shear waves).

We show by a simple calculation that it is the interaction of the impurity molecule with the longitudinal phonon which leads to an enhanced trapping of the impurity in the soft tail region and hence to a much larger effective mass of the impurity along the preferred direction which is responsible for the large anisotropy in the impurity diffusion.

III THEORY

We now introduce the dilation operator $\Delta(\mathbf{x})$ describing lattice deformation and the corresponding acoustic phonon mode along preferred direction[6]

$$\Delta(\mathbf{x}) = i \sum_{\mathbf{q}} (2\rho\hbar\omega_{\mathbf{q}} V)^{-1/2} \hbar |\mathbf{q}| [b_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{x}} - b_{\mathbf{q}}^{+} e^{-i\mathbf{q}\cdot\mathbf{x}}] \tag{5}$$

where $\mathbf{q}$ and $\omega_{\mathbf{q}}$ are respectively the phonon wavevector and angular frequency, $b_{\mathbf{q}}$ and $b_{\mathbf{q}}^{+}$, the phonon annihilation and creation operators with wavevector $\mathbf{q}$, ρ the density of the host liquid crystal, V the volume over which the periodic boundary conditions are imposed, and $\hbar = h/2\pi$ (h = Planck's constant). We also introduce the field operators for the impurity

$$\psi(\mathbf{x}) = \sum_{\mathbf{k}} c_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{x}} u_{\mathbf{k}}(\mathbf{x}),$$

and

$$\psi^{+}(\mathbf{x}) = \sum_{\mathbf{k}} c_{\mathbf{k}}^{+} e^{-i\mathbf{k}\cdot\mathbf{x}} u_{\mathbf{k}}^{*}(\mathbf{x}) \tag{6}$$

where $c_{\mathbf{k}}$ and $c_{\mathbf{k}}^{+}$ are respectively the annihilation and creation operators for the impurity with wavevector $\mathbf{k}$ and $u_{\mathbf{k}}(\mathbf{x})$ is the Bloch wavefunction.

Since we assume that the impurity molecule interacts with the acoustic phonons in the preferred direction of the host molecules in smectic A phases, the interaction Hamiltonian H' for this impurity is given by

$$\begin{aligned} H' &= \int d\mathbf{x}\psi^{+}(\mathbf{x})C_1\Delta(\mathbf{x})\psi(\mathbf{x}) \\ &= iC_1\sum_{\mathbf{k},\mathbf{q}}(2\rho\hbar\omega_{\mathbf{q}}V)^{-1/2}\hbar|\mathbf{q}| \\ &\quad\cdot[b_{\mathbf{q}}c_{\mathbf{k}+\mathbf{q}}^{+}c_{\mathbf{k}} - b_{\mathbf{q}}^{+}c_{\mathbf{k}-\mathbf{q}}c_{\mathbf{k}}], \end{aligned} \tag{7}$$

where C_1 is a constant having the units of energy which can be determined by pressure measurements. Here we note that we have considered only the first order impurity-phonon scattering process and neglected the phonon-phonon interaction which may be important for the self-diffusion of the host molecules. The impurity-impurity interaction is also neglected because of the low impurity concentration.

The impurity-phonon interaction energy to second order in perturbation theory is

$$\Delta E = \langle \mathbf{k}, n_{\mathbf{q}}|H'|\mathbf{k}, n_{\mathbf{q}}\rangle + \sum_{\mathbf{k}', n_{\mathbf{q}'}} \frac{|\langle \mathbf{k}', n_{\mathbf{q}'}|H'|\mathbf{k}, n_{\mathbf{q}}\rangle|^2}{\varepsilon(\mathbf{k}) + \hbar\omega_{\mathbf{q}}n_{\mathbf{q}} - \varepsilon(\mathbf{k}') - \hbar\omega_{\mathbf{q}'}n_{\mathbf{q}'}} \tag{8}$$

Here $|\mathbf{k}\rangle$ is the state of the impurity having wavevector $\mathbf{k}$, and $|n_{\mathbf{q}}\rangle = |n_{\mathbf{q}_1}, \ldots, n_{\mathbf{q}_2}, \ldots, n_{\mathbf{q}_i}, \ldots\rangle$ represents the state of the phonon field in which the number $n_{\mathbf{q}_1}$ of phonons with wavevector $\mathbf{q}_1$, $n_{\mathbf{q}_2}$ with wavevector $\mathbf{q}_2$ etc. are present. The occupation number $n_{\mathbf{q}_i}$ of phonons having wavevector $\mathbf{q}_i$ is given by

$$n_{\mathbf{q}_i} = \frac{1}{\exp(-\beta\hbar\omega_{\mathbf{q}_i})} \tag{9}$$

(In Eq. (8) an ensemble average corresponding to finite temperature phonon field is implied.) The energies $\varepsilon(\mathbf{k})$ and $\hbar\omega_{\mathbf{q}}n_{\mathbf{q}}$ are, respectively, those of the impurity in the unperturbed state $|\mathbf{k}\rangle$ and the phonon field. Because of the form of H', only the intermediate states in which a single phonon is either emitted or absorbed contribute. After calculating the appropriate matrix elements, Eq. (8) reduces to

$$\Delta E(\mathbf{k}) = \frac{C_1^2}{2\rho V}\sum_{\mathbf{q}}\frac{\hbar q^2}{\omega_{\mathbf{q}}}\left[\frac{n_{\mathbf{q}}+1}{\varepsilon(\mathbf{k}) - \varepsilon(\mathbf{k}-\mathbf{q}) - \hbar\omega_{\mathbf{q}}} + \frac{n_{\mathbf{q}}}{\varepsilon(\mathbf{k}) - \varepsilon(\mathbf{k}+\mathbf{q}) + \hbar\omega_{\mathbf{q}}}\right] \tag{10}$$

Since these phonons are present only along the preferred direction of molecular alignment, $\sum_{\mathbf{q}}$ can be replaced by one-dimensional integration

$$\frac{\mathrm{d}}{2\pi}\int_{-q_0}^{q_0} \mathrm{d}q_z \quad \text{where} \quad q_0 = \frac{2\pi}{\mathrm{d}}$$

is the Debye wavevector. For acoustic phonons we approximate $\omega_{\mathbf{q}}$ by vq_z, v being the sound velocity in the host liquid crystal. Integration can now be performed when $k_B T \gg \hbar\omega_{\mathbf{q}}$. In this limit, Eq. (9) for phonon occupation number reduces to $n_{\mathbf{q}_i} = \dfrac{k_B T}{\hbar\omega_{\mathbf{q}_i}}$ and Eq. (10) can be written as

$$\Delta E(k_z) = -\frac{mC_1^2}{2\pi a^2 \rho \hbar v} \ln\left[\frac{2mv + \hbar q_0 - 2\hbar k_z}{2mv - \hbar q_0 - 2\hbar k_z}\right]\left(1 - \frac{k_B T}{2mv^2 - 2\hbar v k_z}\right) \tag{11}$$

Note that if the initial state of the phonon field is taken to be vacuum state, the term involving $k_B T/2(mv^2 - \hbar v k_z)$ in Eq. (11) will be absent. In our case, this term contributes less than 3% to the total impurity–phonon interaction energy $\Delta E(k_z)$. In the longwavelength limit $k_z \cong 0$, Eq. (11) becomes

$$\Delta E(0) = -\frac{mC_1^2}{2\pi a^2 \rho \hbar v} \ln \frac{2mv + \hbar q_0}{2mv - \hbar q_0} \tag{12}$$

The energy given by Eq. (11) of the impurity is in addition to the impurity potential assumed to be of the simple form

$$V(z) = -V_0 \cos\left(\frac{2\pi z}{\mathrm{d}}\right). \tag{13}$$

Here, V_0 is a potential parameter which can be calculated in terms of the molecular parameters and order parameters by using the mean field theory and McMillan's potentials[7] for smectic A phases. Since $\Delta E(k_z)$ is negative, the net effect of the impurity interaction with the longitudinal acoustic mode is the increased trapping of the impurity molecule, thereby making the impurity diffusion along the preferred direction more difficult.

Using the jump diffusion model, the impurity diffusion coefficient along the preferred direction

$$D_{\parallel} = \alpha v\, \mathrm{d}^2 \exp\left(-\frac{Q}{k_B T}\right), \tag{14}$$

where the activation energy Q is now increased from $2V_0$ to $2V_0 + |\Delta E(0)|$, ($2V_0$ being the depth of the potential in Eq. (13)) leading to decreased diffusion. Here α is the geometric jump factor ($=1$ for our case) and v is the vibrational

frequency of the impurity molecule in the potential well, and is given by

$$\nu \cong \frac{1}{d}\sqrt{\frac{V_0}{m}}. \tag{15}$$

Thus the jump frequency Γ for the impurity diffusion is

$$\Gamma \simeq \nu \exp[-(2V_0 + |\Delta E(0)|)/k_B T] \tag{16}$$

The effective mass $m_{\|}$ is now obtained from the energy spectrum Eq. (11) of the impurity molecule from

$$\frac{1}{m_{\|}} = \frac{1}{\hbar^2}\frac{d^2E(k_z)}{dk_z^2}\bigg|_{k_z=0} = \frac{1}{m} - \frac{2mC_1^2}{\pi a^2 \rho \hbar v} \times [(2mv - \hbar q_0)^{-2} - (2mv + \hbar q_0)^{-2}]. \tag{17}$$

In order to determine $m_{\perp}$, the effective mass of the impurity molecule in the soft tail region of the fluid, we use the standard result of a sphere moving in a viscous medium.[8] Thus we can write

$$m_{\perp} = m + \tfrac{2}{3}\pi\rho_0 r^3, \tag{18}$$

where ρ_0 is the average density of the segments in the alkyl chain (soft tail) region. Therefore, the anisotropy ratio, Eq. (4), of the impurity diffusion coefficients parallel and perpendicular to the preferred direction of the smectic A phase of the liquid crystal can be written as

$$\frac{D_{\|}}{D_{\perp}} = \left[m + \frac{2\pi}{3}\rho_0 r^3\right] \times \left[\frac{1}{m} - \frac{2mC_1^2}{\pi a^2 \rho \hbar v}\{(2mv - \hbar q_0)^{-2} - (2mv + \hbar q_0)^{-2}\}\right]. \tag{19}$$

Clearly, from Eqs. (17) and (18), both $m_{\|}$ and $m_{\perp}$ are greater than m, the mass of the sphere. If the coupling constant C_1, which describes the strength of the impurity interaction with the longitudinal acoustic mode is large, it is easy to see that $m_{\|} > m_{\perp}$, so that the anisotropy ratio $D_{\|}/D_{\perp} < 1$.

IV DISCUSSION

In order to get numerical estimates for the anisotropy ratio of the impurity diffusion, we need to estimate the constant C_1, in the interaction Hamiltonian H', Eq. (7) of the impurity molecule with longitudinal acoustic phonon mode. This constant can, for example, be estimated by fitting Eq. (14) to the experimental data on the diffusion coefficient.

For the system studied in the experiments of Murphy *et al.*[4] (TMS in BBOA) the following values are used:

$$T = 53°\text{C}, \quad v \cong 10^5 \text{ cm/sec} \quad \rho = 1 \text{ gm/cm}^3,$$
$$\rho_0 \cong 0.83 \text{ gm/cm}^3, \quad q_0 \approx 2.51 \times 10^7 \text{ cm}^{-1}, \quad m = 1.22 \times 10^{-22} \text{ gm}$$
$$r \simeq 2.1 \times 10^{-8} \text{ cm} \quad \text{and} \quad C_1/a \simeq 3.7 \times 10^{-5} \text{ erg/cm}$$

Substituting these values into Eq. (19), we have

$$\frac{D_\perp}{D_\parallel} = 8.6. \tag{20}$$

The agreement with the experimentally measured[4] anisotropy ratio of 10 for the impurity diffusion is surprising in view of the simplicity of our model.

However, we can be sure that the treatment of the smectic A phase as a crystalline solid along the preferred direction is reasonable. Further, it is a reasonable assumption that the impurity interaction with the longitudinal acoustic phonon mode is responsible for the anisotropy in the diffusion coefficient. Finally, we believe the model can be easily applied to the other highly ordered states, such as the smectic B phase of the liquid crystals.

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