Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Molecular orientational motion in discotic liquid crystals

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To cite this Article Richards, G. M. and Dong, Ronald Y.(1989) 'Molecular orientational motion in discotic liquid crystals', Liquid Crystals, 5: 3, 1011 — 1018

To link to this Article: DOI: 10.1080/02678298908026405

URL: http://dx.doi.org/10.1080/02678298908026405

LIQUID CRYSTALS, 1989, VOL. 5, NO. 3, 1011–1018

Molecular orientational motion in discotic liquid crystals

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The spectral densities of motion for the aromatic and chain deuterons of the discotic mesogen hexahexyoxytriphenylene (THE6) have been reported in the literature for a frequency of 46 MHz. Most spectral densities $J_p(p\omega_0, 90°)$ have been obtained from samples consisting of a planar distribution of domains in which the directors were perpendicular to the magnetic field. Limited data $J_p(p\omega_0)$ have also been available from single-domain samples with the director aligned parallel to the magnetic field. We have applied the small-step rotational diffusion model of Nordio *et al.* to the data from the aromatic deuterons of THE6-ard in its uniaxial columnar D_{ho} phase, to describe the spinning ($D_\parallel$, rotational diffusion constant about the planar normal to the disc) and the tumbling ($D_\perp$, rotational diffusion constant of the planar normal) motions of the molecular core. Although this model has been successfully used for rod-like nematic liquid crystals, its use has not been attempted for discotic liquid crystals. The model seems to indicate that molecular reorientation has slowed down in the D_{ho} phase, giving frequency dependence to the spectral densities. This can be explained by the high orientational order of the molecules. We are able to account for the four spectral densities $J_1(\omega_0)$, $J_1(\omega_0, 90°)$, $J_2(2\omega_0)$ and $J_2(2\omega_0, 90°)$ with a calculated ratio $D_\parallel/D_\perp$ of about 1. This is quite different from that of rodlike liquid crystals.

1. Introduction

Recent deuterium N.M.R. (D.M.R.) relaxation studies [1–12] of thermotropic liquid crystals have clearly established that liquid-crystalline molecules cannot be idealized by a rigid rod or disc. Furthermore, these studies have shown that measurements of individual spectral densities of motion $J_p(\omega)$ at various sites on a molecule can be valuable in probing reorientation and internal motions of flexible molecules in anisotropic mesophases. When models of molecular reorientation and segmental isomerism are used, these spectral densities of motion may also be used to characterize [13] relaxation mechanisms other than reorientational sources, such as fluctuations [14] of the nematic director **n**. Therefore the temperature and frequency dependences of these spectral parameters can provide a searching test for any proposed motional models for liquid crystals.

In general, both overall and segmental motions of a molecule and director fluctuations are responsible for the deuteron spin–lattice relaxation in liquid crystals. The director fluctuations are collective thermal fluctuation modes of the liquid-crystalline molecules. When the director is aligned along the magnetic field, they contribute only to the spectral density $J_1(\omega)$ provided that these fluctuations have small amplitude, and can be identified through a unique frequency dependence [14]. The segmental motions in an alkyl chain [12, 13] and the internal phenyl-ring rotation [10] of rod-like liquid crystals have recently been treated by a superimposed-rotations model. The reorientation of a mesogenic molecule in a potential of mean torque may be modelled by the small-step rotational diffusion (S.S.R.D.) model proposed by Nordio and

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coworkers [15–17]. Recent D.M.R. studies [13, 18] of rodlike mesogens appear to support the application of the S.S.R.D. model.

In this paper we apply the S.S.R.D. model to a discotic liquid crystal, hexahexyloxytriphenylene (THE6), by considering the aromatic deuterons in a ring-deuterated THE6-ard. The triphenylene core is rigid and its deuterated aromatic sites are to a first approximation only sensitive to reorientation of the disc-like core. THE6 exhibits a columnar (D_{ho}) phase in which the molecules are stacked into columns, which in turn are arranged into two dimensional arrays. Since the diamagnetic susceptibility anisotropy $\Delta\chi < 0$ for a THE6 sample, the molecules are ordinarily aligned with the local directors $\mathbf{n}$ perpendicular to the external magnetic field (see figure 1). Two types of samples [5] were prepared to allow measurements of the relaxation rates with the magnetic field perpendicular ($\theta = 90°$) and parallel ($\theta = 0°$) to the directors. Goldfarb *et al.* [5] have reported four experimental spectral densities $J_1(\omega_0, 0°) \equiv J_1(\omega_0)$, $J_2(2\omega_0, 0°) \equiv J_2(2\omega_0)$, $J_1(\omega_0, 90°)$ and $J_2(2\omega_0, 90°)$ at several temperatures in the columnar phase of THE6. It is found that in THE6, $J_1(\omega_0)$ is less than $J_2(2\omega_0)$, which is the reverse of observations in rod-like mesogens [3, 4, 6–11]. So far, molecular reorientation has been found to be in the fast-motion limit in most rod-like mesogens. Because of the high degree of molecular order ($\overline{P_2} \geqslant 0\cdot9$) in the columnar phase, molecular reorientation is expected to be slow, thereby introducing frequency dependence in the spectral densities of motion. The spectral densities

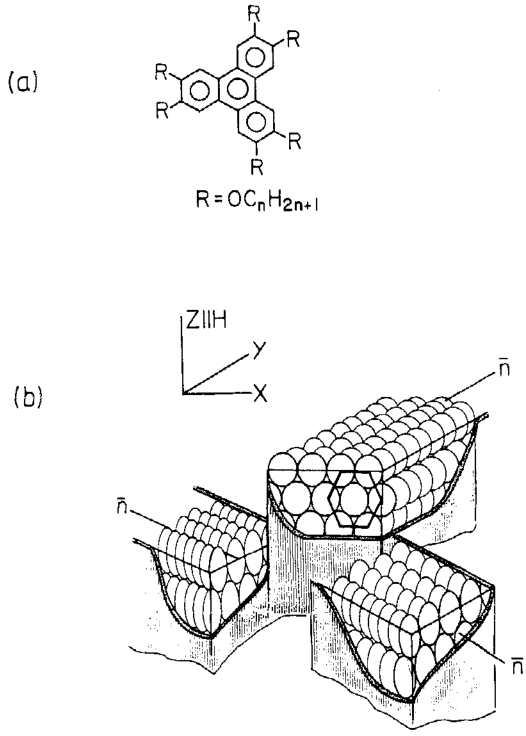

Figure 1. (*a*) Molecular structure of THE*n*. (*b*) Schematic diagram of the domain distribution in a sample formed by cooling in a magnetic field from the isotropic phase. The discs represent the mesogens and the $\hat{\mathbf{n}}$s are the directors of the various domains. They lie in the *xy* plane while the magnetic field is parallel to the *z* axis.

$J_p(p\omega_0, 90°)$ can be related to the spectral densities $J_p(p\omega_0)$ [19, 20] by

$$J_1(\omega_0, 90°) = \tfrac{1}{2}[J_1(\omega_0) + J_2(\omega_0)], \tag{1}$$

$$J_2(2\omega_0, 90°) = \tfrac{3}{8}J_0(2\omega_0) + \tfrac{1}{2}J_1(2\omega_0) + \tfrac{1}{8}J_2(2\omega_0). \tag{2}$$

As the spectral densities at $\theta = 90°$ involve $J_p(\omega)$ at two different frequencies, ω_0 and $2\omega_0$, the frequency dependence of molecular reorientation can be examined.

2. Theory

For a spin-1 deuteron, the spectral density is given by the cosine transform of the autocorrelation function $G_{m_\mathrm{L}}(\mathrm{t})$

$$J_{m_\mathrm{L}}(m_\mathrm{L}\omega) = \frac{3\pi^2}{2}\left(\frac{e^2qQ}{h}\right)^2 \int_0^\infty G_{m_\mathrm{L}}(t)\cos(m_\mathrm{L}\omega t)\,dt, \tag{3}$$

where e^2qQ/h is the quadrupolar coupling constant and

$$G_{m_\mathrm{L}}(t) = \sum_{m_\mathrm{M}} |d^2_{m_\mathrm{M}0}(\beta_{\mathrm{M,Q}})|^2 g_{m_\mathrm{L}m_\mathrm{M}}(t), \tag{4}$$

with $g_{m_\mathrm{L}m_\mathrm{M}}(t)$ being given by

$$g_{m_\mathrm{L}m_\mathrm{M}}(t) = \langle (D^2_{m_\mathrm{L},m_\mathrm{M}}(0) - \overline{D^2_{m_\mathrm{L},m_\mathrm{M}}})(D^{2*}_{m_\mathrm{L},m_\mathrm{M}}(t) - \overline{D^{2*}_{m_\mathrm{L},m_\mathrm{M}}})\rangle. \tag{5}$$

The Wigner rotation-matrix elements $D^2_{m_\mathrm{L},m_\mathrm{M}}(\Omega)$ relate the second-rank tensor components in the laboratory and molecular fixed frames, which appear in the relaxation Hamiltonian. The subscripts m_L and m_M are the projection indices for these tensor components in the laboratory and molecular frames respectively. $\beta_{\mathrm{M,Q}}$ is the angle between the C–D bond and the molecular symmetry (z_M) axis. For THE6, the z_M axis is taken to be normal to the discotic core. In treating a rigid mesogen reorienting in a uniaxial phase, the potential of mean torque may be approximated by $U(\beta_0)/kT = -\lambda P_2(\cos\beta_0)$. The small-step rotational diffusion model used to evaluate the autocorrelation functions involves solving [15–17] the rotational diffusion equation under the above restoring pseudopotential.

The single-particle distribution function $f(\beta_0)$ is given by

$$f(\beta_0) = \frac{\exp[-U(\beta_0)/kT]}{Z}, \tag{6}$$

where the partition function Z is

$$Z = \int_0^\pi \exp\left[-\frac{U(\beta)}{kT}\right]\sin\beta\,d\beta. \tag{7}$$

Given $f(\beta_0)$, equilibrium properties such as order parameters $\overline{P_2} \equiv \langle D^2_{00}(\Omega_0)\rangle$ and $\overline{P_4} \equiv \langle D^4_{00}(\Omega_0)\rangle$ may be evaluated for the mesophase, where Ω_0 are the Euler angles describing the instantaneous orientation of the molecule in the liquid-crystalline coordinate system. The autocorrelation functions $g_{m_\mathrm{L}m_\mathrm{M}}(t)$ are in general given by an infinite sum of decreasing exponentials [21]. However, in most cases one can approximate by retaining the first term in the sum. In particular, it is given [22] by a single exponential in the limit of perfect order. Thus one has

$$g_{m_\mathrm{L}m_\mathrm{M}}(t) = \kappa(m_\mathrm{L}, m_\mathrm{M})\exp\left(-\frac{t}{\tau^{(2)}_{m_\mathrm{L}m_\mathrm{M}}}\right), \tag{8}$$

where the correlation times $\tau^{(2)}_{m_L m_M}$ are given in terms of an axially symmetric rotation diffusion tensor whose principal values are $D_\parallel$, the rotation diffusion constant about the molecular symmetry axis, and $D_\perp$, the rotation diffusion constant of this axis,

$$(\tau^{(2)}_{m_L m_M})^{-1} = \frac{D_\perp}{\lambda^{(2)}_{m_L m_M}} + m_M^2(D_\parallel - D_\perp) \tag{9}$$

and $\lambda^{(2)}_{m_L m_M}$ are given in the table in terms of the deviation from perfect alignment $\delta = 1 - \overline{P_2}$. The $\kappa(m_L, m_M)$ are the mean squares of the Wigner rotation matrices,

$$\kappa(m_L, m_M) = \langle [D^2_{m_L, m_M}(\Omega_0)]^2 \rangle - |\langle D^2_{m_L, m_M}(\Omega_0)\rangle|^2 \delta_{m_L 0}\delta_{m_M 0}, \tag{10}$$

and can be expressed [20] in terms of the order parameters $\overline{P_2}$ and $\overline{P_4}$ (see the table). In the limit of perfect alignment, $\kappa(m_L, m_M)$ take the form of $C(m_L, m_M)$ [22], which are given in the table. Using equations (4) and (8) in equation (3), one obtains the spectral density of motion for a deuteron on a rigid core of a reorienting mesogen,

$$J_{m_L}(\omega) = \frac{3\pi^2}{2}\left(\frac{e^2qQ}{h}\right)^2 \sum_{m_M} |d^2_{m_M 0}(\beta_{M,Q})|^2 \kappa(m_L, m_M) \frac{[\tau^{(2)}_{m_L m_M}]^{-1}}{[\tau^{(2)}_{m_L m_M}]^{-2} + \omega^2}, \tag{11}$$

where the sum over m_M is between -2 and $+2$.

Expressions for $\kappa(m_L, m_M)$ in terms of $\overline{P_2}$ and $\overline{P_4}$, and $C(m_L, m_M)$ and $\lambda^{(2)}_{m_L m_M}$ in terms of $\delta = 1 - \overline{P_2}$ (reproduced from [20, 21]).

$\lvert m_L \rvert$	$\lvert m_M \rvert$	$\kappa(m_L, m_M)$†	$C(m_L, m_M)$†	$\lambda^{(2)}_{m_L m_M}$
0	0	$\frac{1}{5} + \frac{2}{7}\overline{P_2} + \frac{18}{35}\overline{P_4} - (\overline{P_2})^2$	0	—‡
1	0	$\frac{1}{5} + \frac{1}{7}\overline{P_2} - \frac{12}{35}\overline{P_4}$	δ	$\frac{1}{3}\delta$
2	0	$\frac{1}{5} - \frac{2}{7}\overline{P_2} + \frac{3}{35}\overline{P_4}$	0	—
1	1	$\frac{1}{5} + \frac{1}{14}\overline{P_2} + \frac{8}{35}\overline{P_4}$	$\frac{1}{2}(1 - \frac{5}{3}\delta)$	1
1	2	$\frac{1}{5} - \frac{1}{7}\overline{P_2} - \frac{2}{35}\overline{P_4}$	$\frac{1}{3}\delta$	$\delta/(3 + 2\delta)$
2	2	$\frac{1}{5} + \frac{2}{7}\overline{P_2} + \frac{1}{70}\overline{P_4}$	$\frac{1}{2}(1 - \frac{2}{3}\delta)$	$\frac{1}{4}$

† $\kappa(m_L, m_M) = \kappa(m_M, m_L)$ and $C(m_L, m_M) = C(m_M, m_L)$.
‡ Since $C(m_L m_M)$ is zero, the corresponding $\lambda^{(2)}_{m_L m_M}$ is not required.

For the aromatic deuterons in THE6, $\beta_{M,Q} = 90°$ and the quadrupolar coupling constant is 183 kHz. In applying equation (11) to calculate the spectral densities of motion, one is faced with the choice of either $\kappa(m_L, m_M)$ or $C(m_L, m_M)$. The difficulty in using $\kappa(m_L, m_M)$ is related to the uncertainty in the value of $\overline{P_4}$, which has not been measured experimentally for THE6, while $C(m_L, m_M)$ are asymptotic expressions. $\overline{P_2}$ is calculated from the quadrupolar splitting [23] of the aromatic deuterons and $\overline{P_4}$ is approximated by using the Maier–Saupe potential [24, 25] for nematogens (i.e. $\lambda = T_c\overline{P_2}/(0{\cdot}2202T)$, where T_c is the clearing temperature) and Gaussian integration. Using the $\overline{P_2}$ and $\overline{P_4}$ ($\geqslant 0{\cdot}4$) values, $\kappa(0, 0)$ and $\kappa(2, 0)$ are found to be negative and therefore set to zero in accordance with $C(0, 0)$ and $C(2, 0)$. $\kappa(2, 2)$ and $C(2, 2)$ are almost identical, while the Cs are less than κs for $m_L = 1$, $m_M = 0$ and $m_L = 1$ and $m_M = 2$. We have examined both $\kappa(m_L, m_M)$ and $C(m_L, m_M)$, and found that in general the experimental spectral densities of THE6 are incompatible with the use of $C(m_L, m_M)$, mainly because of the smaller values of $C(1, 0)$ and $C(1, 2)$.

3. Results and discussion

Figure 1 shows the molecular structure of THE6. In figure 2 we reproduce the experimental data [5] for the deuterons of THE6-ard at a Larmor frequency of 46 MHz. Because of the experimental difficulty in obtaining and retaining single-domain samples with the director aligned along the magnetic field, there are only three temperatures in the intermediate temperature range (between 69°C and 81°C) at which all four spectral densities $J_1(\omega_0)$, $J_2(2\omega_0)$, $J_1(\omega_0, 90°)$ and $J_2(2\omega_0, 90°)$ are available. Since there are only two model parameters $D_\parallel$ and $D_\perp$ in the S.S.R.D. model, any two spectral densities of the above set may be used to derive their values. For the limited temperature range, we may use the derived $D_\parallel$ and $D_\perp$ to calculate the two remaining spectral densities for comparison with their experimental values.

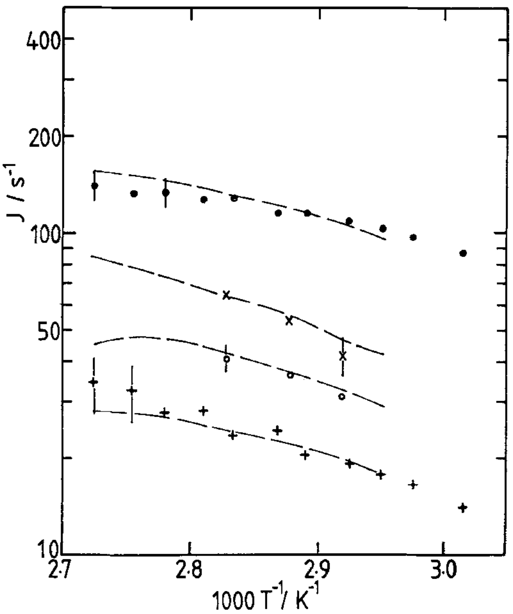

Figure 2. Plots of spectral densities of motion versus the reciprocal temperature: o, x, o, $J_1(\omega_0)$; x, $J_2(2\omega_0)$; •, $J_1(\omega_0, 90°)$; +, $J_2(2\omega_0, 90°)$; – – –, theoretical curves from the small-step rotational diffusion model.

We have rewritten $J_0(\omega)$, $J_1(\omega)$ and $J_2(\omega)$ of equation (11) in terms of $R = D_\parallel/D_\perp$ and $D_\perp$. Using the above Js and the experimental $J_1(\omega_0, 90°)$ and $J_2(2\omega_0, 90°)$ in equations (1) and (2), one obtains two complex equations ($f(R, D_\perp) = 0$ and $g(R, D_\perp) = 0$) involving the two unknowns R and $D_\perp$. These two equations are solved numerically using Newton's method [26] to give R and $D_\perp$. At the same time, the calculated $J_1(\omega_0)$ and $J_2(2\omega_0)$ can be compared with their experimental values. In the intermediate temperature range we have chosen to find $D_\parallel$ and $D_\perp$ so as to give optimum fit to all four spectral densities by minimizing the sum squared relative error $\Sigma_i[(J_i^{\mathrm{expt}} - J_i^{\mathrm{calc}})/J_i^{\mathrm{expt}}]^2$. For temperatures above and below the intermediate temperature range, where only the spectral densities for the 90° orientation are available, these spectral densities may not yield solutions for $D_\parallel$ and $D_\perp$. In this case certain experimental errors are allowed for $J_1(\omega_0, 90°)$ and $J_2(2\omega_0, 90°)$ in the numerical computation in order to enable the S.S.R.D. model to give a solution. In figure 2 we also show the best fit (dashed lines) of the S.S.R.D. model to the experimental data in and above the intermediate temperature range. The derived $D_{\parallel}$ and $D_{\perp}$ from the perpendicular data can be used to predict $J_1(\omega_0)$ and $J_2(2\omega_0)$ for the parallel orientation at high temperatures, as shown in the diagram. It would be of interest to compare these predictions with experimental data. The rotational diffusion constants $D_{\parallel}$ and $D_{\perp}$ are summarized in figure 3. It is interesting to note that the R value was found to be less than unity at low temperatures.

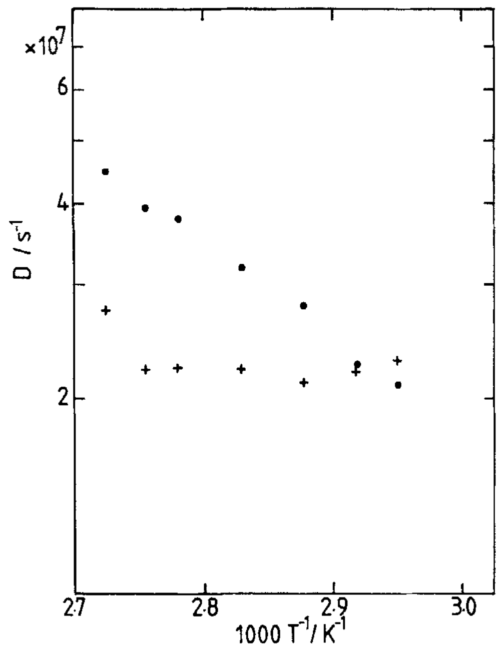

Figure 3. The temperature dependences of the rotational diffusion constants in the columnar phase of THE6: ●, $D_{\parallel}$, +, $D_{\perp}$.

In order to explain both spectral densities of motion for the parallel and perpendicular orientations, the molecular reorientations for THE6 must be slow ($\omega\tau^{(2)}_{m_L m_M} > 1$) on the D.M.R. time scale so as to produce a frequency dependence in the spectral densities of motion. Although both $J_1(\omega)$ and $J_2(\omega)$ are frequency-dependent, $J_1(\omega)$ has relatively smaller frequency dependence, while $J_2(0) \gg J_2(\omega_0) > J_2(2\omega_0)$, in agreement with experiment [5]. This strong frequency dependence is only possible when the anisotropic rotation diffusion factor R is small, i.e. near unity in the intermediate temperature range. This is in contrast with the much larger R value for rodlike mesogens [10, 11, 13, 18]. The low R value for THE6 is not surprising in view of the disc shape of these molecules and, in particular, possible dimer formation [27] from theoretical considerations. It should be noted that director fluctuations [14] would not account for the strong frequency dependence in $J_2(\omega)$ required above. As seen in figure 2, the fit between the theory and experiment is good in the intermediate temperature range, where both parallel and perpendicular orientation data were available. Above this temperature range, although the calculated $J_1(\omega_0, 90°)$ and $J_2(2\omega_0, 90°)$ lie within the error limits of the experimental values, there is a systematic trend that $J_1^{\mathrm{expt}}(\omega_0, 90°)$ is less than its theoretical value, while for $J_2^{\mathrm{expt}}(\omega_0, 90°)$ the opposite is the case. In figure 3 it is seen that $D_\parallel$ obeys an Arrhenius temperature dependence with an activation energy $E_a = 28$ kJ/mol, while $D_\perp$ has a constant value of about $2{\cdot}2 \times 10^{-7}\,\mathrm{s}^{-1}$. The constant $D_\perp$ value, however, is not desirable, and this may indicate the weakness of using the S.S.R.D. model alone or of the assumptions used in the S.S.R.D. model.

Although one may invoke director fluctuations, we do not feel that the limited experimental information would allow a definitive assessment of its contribution. Furthermore, there are limitations in the model [15–17] used to describe molecular reorientation in a columnar phase. The Maier–Saupe potential used in the S.S.R.D. model and in evaluating $\overline{P_4}$ for $\kappa(m_L, m_M)$ is good for nematogens, but its applicability to highly ordered columnar phases may not be appropriate. Theoretical treatment of the rotational diffusion equation with a McMillan-type potential [25] may be required to improve the fit between theory and experiment.

In conclusion, we have demonstrated that the S.S.R.D. model of Nordio *et al.* can be applied to THE6 with limited success. Although the model involves many assumptions and approximations that may not be exact for discotigens, more experimental data are needed to properly assess the model and other models of molecular dynamics in discotic liquid crystals. To this end, one may determine the spectral densities of motion at different Larmor frequencies and/or their angular dependences. As demonstrated in this paper, the parallel-orientation data of THE6 were important in obtaining the model parameters, and more of these are needed over a wider temperature range. Recently, an electric field has been used to orient the director along the external magnetic field for samples with negative diamagnetic anisotropy (unpublished data from R. Y. Dong, J. W. Emsley and K. Hamilton). This may solve some of the difficulty associated with the single-domain sample of THE6 at high and low temperatures.

The financial support of the Natural Sciences and Engineering Council of Canada is gratefully acknowledged.

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