Reorganization energy of intermolecular electron transfer in solvents near isotropic/nematic transition

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Monte Carlo simulations of the fluid of dipolar spherocylinders have been carried out to produce structure factors of longitudinal polarization fluctuations in the region of orientational isotropic/nematic phase transition. These data are used to calculate the solvent reorganization energy of intermolecular electron transfer. The reorganization energy shows substantial anisotropy in the nematic phase in respect to the angle between the direction of electron transfer and nematic director. This anisotropy is sufficient to change the rate of electron transfer by orders of magnitude by reorienting the donor–acceptor complex relative to the nematic director. © 2003 American Institute of Physics. [DOI: 10.1063/1.1580107]

I. INTRODUCTION

The effect of a condensed-phase solvent on the kinetics of electron transfer (ET) reactions is controlled by the coupling of the electric charge of the transferred electron to the nuclear component of the electric potential created by the partial charges on the overall neutral solvent molecules. When the distribution of the solvent molecular charge is approximated by a point dipole, the donor and acceptor electronic states are coupled to the dipolar polarization $P_{\text{tot}} = P_{\text{mac}} + P$. Its macroscopic component $P_{\text{mac}}$ is responsible for the polarization of the liquid as a whole and the microscopic polarization $P$ can be split into the equilibrium part $P_0$ induced by the electric field of the donor–acceptor complex (DAC) and a thermally fluctuating part $\delta P$. Both $P_0$ and $\delta P$ decay on a microscopic lengthscale. On the contrary, the polarization $P_{\text{mac}}$ extends over a macroscopic length scale shifting the donor–acceptor energy gap by the magnitude $\int P_{\text{mac}} \cdot \Delta E_0 \, dr$, where $\Delta E_0 = E_{02} - E_{01}$ is the difference of the vacuum electric fields of the transferred electron in the donor ($E_{01}$) and acceptor ($E_{02}$) states.

The fluctuating nuclear polarization is long range enough to include many solvent molecules. The central limit theorem\(^1\) then requires the field $\delta P$ to obey the Gaussian statistics and one arrives at the Marcus picture of two interacting parabolas.\(^2\) The ET activation barrier is then determined by two parameters: the driving force $\Delta F_0$ and the solvent reorganization energy $\lambda_r$ (intramolecular reorganization\(^3\) is not considered here). The former is the free-energy gap between the equilibrium configurations of the system before and after the reaction, the latter reflects the width of the distribution of the donor–acceptor energy gaps. The macroscopic polarization $P_{\text{mac}}$ and the local equilibrium polarization $P_0$ both affect the driving force, whereas the distribution of polarization fluctuations $\delta P$ affects the reorganization energy.

All currently available models of the solvent effect on ET in homogeneous media limit the consideration to isotropic solvents with (i) $P_{\text{mac}} = 0$ and (ii) isotropic spectrum of polarization fluctuations $\delta P$. At least one of these conditions breaks down if liquid crystalline phase is used as a solvent. A liquid crystal (LC) mesophase is characterized by the disappearance of the orientational disorder without a complete crystalline translational order.\(^4\) Two types of truly liquid LC’s without translational symmetry may exist: ferroelectrics and nematics. Depending on the symmetry of the new mesophase, its creation brings about a nonzero magnitude to an order parameter equal to zero in the high-temperature, symmetric phase.\(^5\) A ferroelectric phase shows a preferential orientation of molecular dipoles reflected by the director unit vector $\hat{n}$ and a nonzero macroscopic polarization $P_{\text{mac}} = \hat{n} P_{\text{mac}} \neq 0$. In the nematic phase, the molecules are also aligned along some preferential direction, but uniaxial symmetry has no polarity leading to the equivalence of $\hat{n}$ and $-\hat{n}$. The order parameter is then a second-rank quantity

$$S_2 = \langle P_2(\hat{\epsilon} \cdot \hat{n}) \rangle,$$

where $P_2(x)$ is the second Legendre polynomial and $\hat{\epsilon}$ is a unit vector of the molecular orientation; $\langle \cdot \cdot \rangle$ represents an ensemble average.

Nematic symmetry generates anisotropy of any second-rank susceptibility of the solvent.\(^4\) In particular, the response function of the solvent polarization

$$\chi_{\alpha\beta}(r,r') = \beta \langle \delta P_{\alpha}(r) \delta P_{\beta}(r') \rangle$$

becomes anisotropic in the nematic phase (\(\alpha\) and $\beta$ subscripts refer to the Cartesian components). The polarization susceptibility is a critical parameter affecting the solvent-induced component of the driving force and the solvent reorganization energy.\(^7\)–\(^11\) An appreciable anisotropy of $\chi_{\alpha\beta}$ should thus project itself into anisotropy of the driving force and reorganization energy in respect to the orientation of the DAC relative to a macroscopic symmetry axis of the solvent. To summarize, both conditions (i) and (ii) above break down in the ferroelectric phase and only condition (ii) breaks down in the nematic phase. This study addresses the second issue.

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We are considering here the variation of the solvent reorganization energy of intermolecular ET when the solvent passes through the isotropic-nematic (IN) phase transition point.

Surprisingly little is known about ET in LC solvents both experimentally and theoretically. LC’s as media for ET reactions have, however, attracted some attention as models of orientational order in photosynthetic reaction centers\cite{12-14} and as media for optimizing the efficiency of photovoltaic devices.\cite{15-16} A few studies report a significant (up to 10^2 times) enhancement of heterogeneous rates for redox proteins immobilized in LC surfactants.\cite{16,17} For homogeneous reactions, an early report of nearly three to four orders of magnitude reduction in the charge separation (CS) rate in LC’s compared to isotropic solvents\cite{15} was followed by more detailed studies by Wąsielewski’s group.\cite{18-20} These studies have shown a dramatic reduction in ET rates when the isotropic phase approaches the IN transition temperature T_{IN}.\cite{19} This effect is, however, observed only for CS in a LC with negative dielectric anisotropy and only for charge recombination (CR) in a LC with positive dielectric anisotropy. Such a dramatic difference may point to a change in equilibrium orientation of the DAC relative to the nematic director, suggesting a substantial effect of solvent anisotropy on either the ET activation barrier or the rate preexponent. Current kinetic measurements\cite{18-20} are limited to the isotropic phase and no ET rates have been reported in the nematic phase. In addition, experiments report the net rate constants only. This limitation does not allow one to distinguish between the variation in the solvent dynamics\cite{21,22} and in the activation barrier when approaching the IN transition point. The understanding of the ET kinetics in the nematic phase still does not exist even on the qualitative level. In the absence of direct experimental evidence, computer experiment can provide first insights into the problem of ET activation in solvents with orientational anisotropy.

The effect of solvent polarization anisotropy in the nematic mesophase on the ET activation energy is the main focus of the current study. The calculation of the solvent reorganization energy is based on the computer simulations of the Fourier transform of the polarization response function $\chi_{ab}$ for a model fluid of hard spherocylinders (HSC’s) (Sec. III). Based on the response function as an input, the solvent reorganization energy is calculated in Sec. IV at various orientations of the DAC relative to the nematic director. We observe a substantial variation of the solvent reorganization energy as a function of the orientation of the DAC. Implementations of this result for controlling the ET rates are discussed in Sec. V.

II. PROBLEM FORMULATION

Within the Marcus formulation of ET activation in polar solvents,\cite{2} the ET solvent reorganization energy, $\lambda_s$, determines the width of the Gaussian distribution of the donor–acceptor energy gaps created by high-temperature nuclear fluctuations of the solvent. In molecular solvents, the magnitude of $\lambda_s$ is affected by such factors as the longitudinal versus transverse polarization of the solvent,\cite{23} nondipolar,\cite{24} and dipolar,\cite{25-27} solvation, and the local solute–solvent density profile (density reorganization).\cite{8} In polar solvents, the orientational fluctuations of the solvent dipoles produce the main contribution to $\lambda_s$.\cite{10,28} Only this component of $\lambda_s$ is considered in this paper. In order to avoid the necessity to include the response of the transverse solvent polarization,\cite{29} we will use a simplified donor–acceptor geometry corresponding to ET between widely separated donor and acceptor units (intermolecular ET). This approximation, going back to studies by Pekar and Marcus,\cite{30,31} assumes that the Fourier transform of the difference vacuum electric field $\Delta \tilde{E}_0$ of the DAC is approximately longitudinal,

$$\Delta \tilde{E}_0(k) = \hat{k} \Delta \tilde{E}_L(k),$$

where the Fourier transform

$$\Delta \tilde{E}_0(k) = \int_\Omega \Delta E_0(r) e^{i\hat{k} \cdot r} dr$$

is defined on the volume $\Omega$ outside the molecular core of the DAC. A longitudinal electric field couples to longitudinal polarization fluctuations of the solvent.\cite{29} The corresponding longitudinal solvent reorganization energy $\lambda_L$ is then given by the Fourier space integral of the solute difference field and the longitudinal response function\cite{10,11,26}

$$\lambda_L = \frac{1}{2} \int \frac{dk}{(2\pi)^3} \chi^L(k) |\Delta \tilde{E}_L(k)|^2,$$

where

$$\chi^L(k) = \frac{1}{\hat{k}} \chi \frac{1}{\hat{k}}$$

and hats are used for unit vectors ($\hat{k} = k/k$). The function $\chi^L(k)$ is not available from experiment and, to the best of our knowledge, has never been obtained for anisotropic liquids. A few computer simulations of the longitudinal response function in model isotropic fluids have been reported in the literature.\cite{32-37} The main goal of the present study is to obtain the longitudinal response function in a pure model LC solvent from computer simulations and use it in Eq. (5) for the calculation of $\lambda_L$. Our focus is on the understanding of the qualitative change in the ET activation barrier in the IN transition region.

III. DIELECTRIC PROPERTIES

The response function of a solvent to an external vacuum field $E_0$

$$\chi_0 = (3\gamma/4\pi) \delta$$

is proportional to the density of point dipoles $\gamma$ and the rank-two spatial correlation function of the dipolar orientations

$$S_{ab}(r) = (3/N) \left( \sum_{i,j} e_{ia} e_{jb} e^{i\hat{k} \cdot r_{ij}} \right)_0.$$

In Eq. (8), $e_{ia}$ is the Cartesian $\alpha$ component of the unitary vector of dipole orientation of the $i$th molecule at the space point $r_i$, $r_{ij} = r_j - r_i$ and the sum runs over the $N$ solvent molecules. The average $\langle \cdots \rangle_0$ is over the equilibrium configurations of the solvent in the presence of the field source (solute). For the solvent of dipolar HSC’s the dipolar density
where $D_k$ is given in terms of the reduced dipole moment $(m^*)^2 = \beta m^2/\sigma^3$ and the length $L$ of the cylindrical part of HSC molecules; $\sigma$ is the diameter of HSC’s and $\eta$ is the packing fraction.

The response function $\chi_0$ is different from the response function $\chi$ characterizing the solvent polarization created by the total electric field within the solvent,88 by the fact that $\chi_0$ depends on the symmetry of the external field and the boundary conditions of the field source, e.g., the shape of the excluded volume created by solute’s insertion.38 This effect is relatively insignificant for solvents polarities considered here.40 Our estimates show that for solvents considered in this publication it is safe to assume that the longitudinal response function is not affected by the boundary conditions and one can replace $(\cdots)_0$ with the equilibrium ensemble average $(\cdots)$ of the bulk solvent:

$$\chi^L(k) = \chi_0^L.$$ (9)

The longitudinal structure factor of dipolar polarization

$$S^L(k) = \hat{k} \cdot S \cdot \hat{k}$$ (10)

depends only on the absolute magnitude of $k$ in the isotropic phase,32,34–36 In the nematic phase, $S^L(k)$ becomes dependent also on the azimuthal angle $\chi$ between $\hat{k}$ and $\hat{n}$ (Fig. 1). Equations (8) and (11) can then be rewritten in the form

$$S^L(k) = 1 + 2S_L P_2(\cos \chi)$$
$$+ \left(6/\langle N \rangle\right) \sum_{i<j} (\hat{e}_i \cdot \hat{k})(\hat{k} \cdot \hat{e}_j)e^{ikr_{ij}}.$$ (12)

At $k=0$, one obtains

$$S^L(0, \cos \chi) = \frac{1}{3} \text{Tr}(S) + \frac{2}{3} \Delta SP_2(\cos \chi),$$ (13)

where $\Delta S = S_0 - S_\perp$, $\text{Tr}(S) = S_0 + 2S_\perp$, $S_0$ and $S_\perp$ refer to $\hat{k} = \hat{n}$ and $\hat{k} = \hat{n}_\perp$ in Eq. (12), respectively; $\hat{n}_\perp$ is a unitary vector perpendicular to $\hat{n}$. Orientational correlations between different molecules disappear at $k \to \infty$, and the last summand in Eq. (12) vanishes. This leads to the $k \to \infty$ asymptote

$$S^L(\infty, \cos \chi) = 1 + 2S_L P_2(\cos \chi),$$ (14)

where the order parameter $S_2$ is given by Eq. (1).

The longitudinal response function of the nuclear polarization $\chi^L(k) = \hat{k} \cdot \chi \cdot \hat{k}$ is connected to the $k$-dependent longitudinal, $\epsilon^L(k)$, and high-frequency, $\epsilon_\infty$, dielectric constants of the solvent.41

$$4 \pi \chi^L(k) = \epsilon_\infty^{-1} - \epsilon^L(k)^{-1},$$ (15)

where $\epsilon_\infty = 1$ in our simulations. Equations (7), (10), (12), and (15) allow us to study the dielectric properties of the solvent in the isotropic and nematic phases from computer simulations.

A. Simulation procedure

The standard Monte Carlo (MC) technique is used to simulate $N = 800$ hard spherocylinders (HSC’s) with embedded point dipoles in the canonical $NVT$ ensemble.42 The phase diagram for this fluid is well documented at the aspect ratio $L/\sigma = 5.43$–48 With increasing the packing fraction $\eta = \rho^*(1 + 3L/2\sigma)$, $\rho^* = \rho \sigma^3$ ($\rho$ is the number density), the isotropic phase loses its stability at about $\eta_{NI} = 0.407$ resulting in the formation of the nematic phase.49 In view of the relatively weak effect of dipolar forces on the transition point,38 changing the solvent packing density is the major tool employed here to drive the solvent from the isotropic to nematic phase.

The simulations are carried out within the reaction-field (RF) cutoff of the long-range dipolar interactions. The RF cutoff was shown to be equivalent to the Ewald summation technique for this particular system46 and is employed here due to its higher computational efficiency. Dynamic adjustment of the dielectric constant of the continuum surrounding the cutoff radius to that generated for the liquid in the course of simulations does not change the observable quantities compared to a constant reaction field and the dielectric constant of $\epsilon_{RF} = 1000$ was adopted for all simulation runs. A cubic simulation box is formed by employing the particular value of the aspect ratio $L/\sigma = 5$ adopted for the fluid of HSC’s. A single layer of $(L/\sigma) = 25 fcc$ cells containing hard spheres of the diameter $\sigma$ in cells’ vertexes was first generated. The spheres were then stretched along the $z$ axis to form a cubic subcell of parallel HSC’s with the aspect ratio $L/\sigma = 5$. The simulation box was filled with $N_c$ of such subcells. With $N_c = 2$ the cubic simulation box contains $N = 4(L/\sigma)^3 N_c = 800$ particles. Point dipoles, randomly oriented along the principle axis, were placed at the inversion center of each spherocylinder.

The isotropic and nematic fluids were created by compression from an initially very small packing fraction $\eta_{start} = 0.001$. Trial MC displacements and orientations with an overlap check after each move were performed to create a completely disordered phase. To reach the target value of $\eta$ the packing fraction was increased from $\eta_{start}$ in small increments, each followed by standard Metropolis equilibration cycles.42 After the target packing density was reached, $NVT$ simulations, consisting of $4 \times 10^5$ equilibration cycles followed by $(6 - 8) \times 10^5$ production runs, have been carried out. The fractions of successful displacements and rotations
were monitored separately with the acceptance ratio 0.4 adopted for both displacements and rotations. To improve the sampling of the phase space and speed up equilibration, a small number of molecules (following Ref. 48, we used five molecules) were randomly chosen at each MC cycle and the direction of their dipoles were reversed within the Metropolis algorithm. The convergence of the equilibration procedure was monitored by periodic calculations of the order parameter \( S_2 \) (Fig. 2), Kirkwood factor \( g_{i,\perp} \), and the two first cumulants of the solvent–solvent interaction energy \( u_{ss} \), from the nematic to smectic-A phase at \((m^*)^2 = 6\). Finally, two angular projections of the pair correlation function on rotational invariants \( \Delta(12) = \hat{e}_1 \cdot \hat{e}_2 \) and \( D_{ij}(12) = 3(\hat{e}_1 \cdot \hat{r})(\hat{e}_2 \cdot \hat{r}) \) were calculated (Fig. 4). Following the standard notation,\(^5\) the angular projections \(h_{110}(r)\) and \(h_{112}(r)\) refer to \(\Delta(12)\) and \(D_{ij}(12)\), respectively.

### B. Dielectric constant

The structure factors obtained from finite-size simulations cannot be directly applied to infinite-size systems since the cutoff of the dipolar potential is propagated through the entire system due to the long-range nature of the dipolar interactions. We used the finite-size correction formalism due to Neumann\(^5\)\(^2\) to obtain the infinite-size \( S^L(k) \) from simulated \( \tilde{S}^L(k) \)

\[
[S^L(k)]^{-1} = [\tilde{S}^L(k)]^{-1} + \frac{18 \gamma \epsilon_{RF} j_1(k r_c)}{2 \epsilon_{RF} + \frac{1}{k r_c}},
\]

where \( r_c \) is the cutoff radius, taken as one-half of the size of the simulation box, and \( j_n(x) \) is the \( n \)-th order spherical Bessel function.\(^5\)\(^3\)

Equation (16), in combination with Eqs. (6), (7), (10), and (15), gives the anisotropic dielectric constant of the fluid. The parallel (\( \hat{k} \) is parallel to \( \hat{n} \)) and perpendicular (\( \hat{k} \) is parallel to \( \hat{n}_\perp \)) components of the dielectric constant were calculated and plotted against the packing density in Fig. 5.

#### TABLE I. Results of MC NVT simulations for \( N = 800 \) dipolar HSC’s with a central longitudinal dipole of \((m^*)^2 = 1.0\). \( \beta(u_{ss}) \) and \( \beta^2(\delta u_{ss})^2 \) denote the first two cumulants of the solvent–solvent interaction energy per particle; \( \epsilon_{i,\perp} \) and \( g_{i,\perp} \) are the dielectric constant and the Kirkwood factor in the directions parallel and perpendicular to the director.

<table>
<thead>
<tr>
<th>( \eta )</th>
<th>( S_2 )</th>
<th>( \epsilon_1 )</th>
<th>( \epsilon_\perp )</th>
<th>( g_1 )</th>
<th>( g_\perp )</th>
<th>( -\beta(u_{ss}) )</th>
<th>( \beta^2(\delta u_{ss})^2 )</th>
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<tr>
<td>0.300</td>
<td>0.045</td>
<td>1.30</td>
<td>1.26</td>
<td>0.97</td>
<td>0.85</td>
<td>-0.065</td>
<td>0.074</td>
</tr>
<tr>
<td>0.330</td>
<td>0.055</td>
<td>1.33</td>
<td>1.28</td>
<td>0.97</td>
<td>0.84</td>
<td>-0.087</td>
<td>0.089</td>
</tr>
<tr>
<td>0.360</td>
<td>0.086</td>
<td>1.35</td>
<td>1.29</td>
<td>0.94</td>
<td>0.79</td>
<td>-0.119</td>
<td>0.124</td>
</tr>
<tr>
<td>0.382</td>
<td>0.101</td>
<td>1.38</td>
<td>1.31</td>
<td>0.95</td>
<td>0.79</td>
<td>-0.134</td>
<td>0.148</td>
</tr>
<tr>
<td>0.395</td>
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<td>1.42</td>
<td>1.29</td>
<td>1.01</td>
<td>0.73</td>
<td>-0.147</td>
<td>0.154</td>
</tr>
<tr>
<td>0.407</td>
<td>0.365</td>
<td>1.65</td>
<td>1.17</td>
<td>1.48</td>
<td>0.43</td>
<td>-0.163</td>
<td>0.165</td>
</tr>
<tr>
<td>0.423</td>
<td>0.591</td>
<td>1.76</td>
<td>1.14</td>
<td>1.64</td>
<td>0.34</td>
<td>-0.158</td>
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<td>1.83</td>
<td>1.10</td>
<td>1.74</td>
<td>0.25</td>
<td>-0.173</td>
<td>0.176</td>
</tr>
<tr>
<td>0.438</td>
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<td>1.83</td>
<td>1.10</td>
<td>1.71</td>
<td>0.24</td>
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<td>0.190</td>
</tr>
<tr>
<td>0.457</td>
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<td>1.98</td>
<td>1.07</td>
<td>1.90</td>
<td>0.15</td>
<td>-0.237</td>
<td>0.269</td>
</tr>
<tr>
<td>0.470</td>
<td>0.850</td>
<td>1.89</td>
<td>1.06</td>
<td>1.70</td>
<td>0.13</td>
<td>-0.229</td>
<td>0.253</td>
</tr>
</tbody>
</table>
The Kirkwood relation provides the parallel and perpendicular projections of the Kirkwood factor also shown in Fig. 5 (closed points),

\[ g_{||\perp} = \frac{(2 \varepsilon_{||\perp} + 1)(\varepsilon_{||\perp} - 1)}{9 \varepsilon_{||\perp}}. \]  

(17)

The dielectric constant is slightly anisotropic in the isotropic phase, probably due to the finite size of the simulation box. It splits into the well-defined parallel and perpendicular component in the nematic phase, as is often observed in experiment (positive anisotropy). The Kirkwood factor behaves in a similar way. Its parallel components increase in the nematic phase pointing to an enhanced correlation of dipoles in the direction parallel to the director. The perpendicular component decays because of antiferroelectric ordering between the neighboring dipoles. This conclusion is supported by the analysis of the distribution function \( h^{110}(r) \) (Fig. 4). Its only peak represents near-contact HSC’s with antiparallel dipoles. The same local structure is responsible for the positive peak of \( h^{112}(r) \). Both functions decay to zero at \( r/\sigma \gg 1 \) indicating the absence of ferroelectric order.

### C. Longitudinal Structure Factor

The calculation of the solvent reorganization energy carried out in Sec. IV below requires the longitudinal structure factor as a function of both the magnitude of the \( \mathbf{k} \) vector and the azimuthal angle between \( \hat{\mathbf{k}} \) and \( \hat{\mathbf{n}} \). These data are hard to extract from finite-size computer simulations since the cubic simulation box imposes a set of discrete eigenvalues on the wave vector \( \mathbf{k} \) to be consistent with the periodic boundary conditions used in the simulations. The director \( \hat{\mathbf{n}} \) is not parallel to any principle axes of the simulation cube and, in addition, fluctuates itself. In view of this, we have calculated \( S^L(k,\cos \chi) \) on a set of \( \mathbf{k} \) vectors in the range \( k\sigma < 50 \) randomly oriented in the plane perpendicular to the director. The azimuthal angle between the director and the \( \mathbf{k} \) vector was varied with the step of 3°. The choice of \( \mathbf{k} \) vectors not belonging to the set of eigenvalues of the simulation box, and the finite size of the simulation box, may generate errors in calculating \( S^L(k,\cos \chi) \). Therefore several consistency checks were performed.

The consistency of calculations of \( S^L(k,\cos \chi) \) from simulations was tested on a few analytical limiting cases. The \( k \to \infty \) limit, given by Eq. (14), is well reproduced when \( S^L(k,\cos \chi) \) levels off at \( k\sigma > 2\pi \) (Fig. 6). At \( k \to 0 \), \( S^L(0,\cos \chi) \) can be obtained from Eq. (13) with \( S_1 \) and \( S_{||\perp} \) from simulations along with a direct calculation from simulated configurations according to the relation

\[
S^L(0,\cos \chi) = 1 + 2S_2 P_2(\cos \chi)
\]

\[ + \left( \frac{6}{N} \right) \sum_{i < j} (\hat{\mathbf{e}}_i \cdot \hat{\mathbf{d}})(\hat{\mathbf{d}} \cdot \hat{\mathbf{e}}_j) \]

(18)

with a set of unitary vectors \( \hat{\mathbf{d}} \) oriented at different angles to \( \hat{\mathbf{n}} \). As is shown in Fig. 7(a), the two approaches essentially coincide in the isotropic phase and in the transition region. However, in the nematic phase, there is an upward deviation of the simulated \( S^L(0,\cos \chi) \) from the theoretical prediction for an infinite system.
The parameter where $D$ is calculated from simulations according to Eq. (18) (points) and from Eq. (13) with $S_i$ and $S_z$ taken from simulations (lines). The function $\Lambda(\cos \chi)$ is calculated as a slope of the linear expansion of the function $F_\phi(\cos \chi)$ in Eq. (22) (points) and according to Eq. (20) using simulated values of $\Lambda(\cos \chi)$ at $\theta=0^\circ$, $45^\circ$, and $90^\circ$ (lines). The parameters are $(m^*)^2=1.0$, $\eta=0.382$ (circles, dashed lines), $0.407$ (diamonds, dot-dashed lines), and $0.457$ (squares, solid lines).

As an additional test of the consistency of our procedure, we have also calculated the second-order expansion coefficient of $S^L(k, \cos \chi)$ in the $k \to 0$ limit

$$S^L(k, \cos \chi) = S^L(0, \cos \chi) + \Lambda^2(\cos \chi)k^2. \quad (19)$$

The parameter $\Lambda(\cos \chi)$ plays the role of the correlation length of the longitudinal polarization fluctuations in the Ornstein–Zernike approximation for the structure factor. An expansion of polarization plane waves in Eq. (12) in spherical harmonics, followed by the angular average in the plane perpendicular to the director, leads to the following form for $\Lambda(\cos \chi)$:

$$\Lambda^2(\cos \chi) = A_0 + A_2 \cos^2 \chi + A_4 \cos^4 \chi \quad (20)$$

with

$$A_0 = -(1/18N) \sum_{i<j} r_{ij}^2 [2\Delta(ij) - D_\Delta(ij)] \times [1 - P_2(\hat{r}_{ij}, \hat{n})],$$

$$A_2 = -(1/6N) \sum_{i<j} r_{ij}^2 [D_\Delta(ij) + 2P_2(\hat{r}_{ij}, \hat{n})] \times [D_\Delta(ij) - \Delta(ij)],$$

$$A_4 = -(1/2N) \sum_{i<j} r_{ij}^2 P_2(\hat{r}_{ij}, \hat{n})D_\Delta(ij), \quad (21)$$

where $D_\Delta(ij) = 3/(\hat{e}_j \cdot \hat{n})(\hat{n} \cdot \hat{e}_i) - \Delta(ij)$. A direct evaluation of $A_0$, $A_2$, and $A_4$ from simulated configuration is poorly convergent due to the factor $r_{ij}^2$. We have therefore calculated $\Lambda^2(\cos \chi)$ as the slope of the linear expansion of the function $F_\phi(\cos \chi)$ in $\delta^2$,

$$F_\phi(\cos \chi) = (3/N) \sum_{i<j} (\hat{e}_i \cdot \hat{k})(\hat{k} \cdot \hat{e}_j)e^{-\delta^2(\hat{k} \cdot r_{ij})^2}. \quad (22)$$

The results of this procedure are shown as points in Fig. 7(b), which are compared to the dependence on $\cos \chi$ from Eq. (20) with the coefficients $A_0$, $A_2$, and $A_4$ evaluated from $\Lambda(\cos \chi)$ taken at $\chi=0^\circ$, $45^\circ$, and $90^\circ$. The two routes to $\Lambda(\cos \chi)$ show a good consistency.

The correlation length of the longitudinal polarization fluctuations as a function of $\eta$ is shown in Fig. 8. This dependence is important in two aspects. First, it shows that the correlation length of the polarization fluctuations is much smaller than the length of the simulation box. Therefore, despite the divergent character of the correlation length of the order-parameter fluctuations at the IN transition point, polarization fluctuations behave normally. Second, polarization fluctuations become essentially uncorrelated, continuumlike at $\chi=90^\circ$. This is certainly consistent with the flat dependence of the structure factor on $k$ at $\chi=90^\circ$ in Fig. 6.

The final test of the calculations of the structure factor involved direct simulations of $S^L(k)$ on the $k$ values consistent with the cubic simulation box. Since the nematic director fluctuates with simulation runs, we have generated a two-dimensional array $S^L(k, \cos \chi)$ directly from simulations. The procedure converges well in the isotropic phase, but gives poor statistics in the nematic phase for the values of $\chi$ not frequently visited by the director. Nevertheless, when the data accumulation converges, the direct simulations on the set of $k$ eigenvalues give results very close to those obtained with a continuous set of wave vectors (Fig. 9). A closer examination of the results suggests, however, that bumps of $S^L(k)$ at small $k$ values can be an artifact of the calculation procedure. Their elimination by smoothing techniques results in uncertainty in the calculated reorganization energies in the range 5–8%.

### IV. ORIENTATIONAL REORGANIZATION ENERGY

With the longitudinal structure factor in hands, we can turn now to the calculation of the solvent reorganization en-
energy according to Eq. (5). In this paper, we assume \( \lambda_s = \lambda_L^2 \) and use the two-sphere Marcus approximation for \( \Delta \tilde{E}^L(k) \),

\[
\Delta \tilde{E}^L(k) = (4\pi e^2/k)\left[j_0(kR_1) - j_0(kR_2)e^{-ikR}\right],
\]

where \( R_1 = R_D + \sigma/2 \) and \( R_2 = R_A + \sigma/2 \) are the distances of the closest approach of solvent hard molecular cores to a spherical donor of the radius \( R_D \) and a spherical acceptor of the radius \( R_A \); \( R \) is the vector pointing from the center of the donor to the center of the acceptor (Fig. 1) and \( e \) is the elementary charge.

The axial symmetry of the LC solvent makes \( \chi^L(k) \) dependent on the azimuthal angle \( \chi \) between \( \mathbf{k} \) and \( \mathbf{n} \). In addition, due to the axial symmetry of the two-sphere DAC, the reorganization energy depends on the azimuthal angle \( \theta \) between the rotation axes of the DAC and \( \mathbf{n} \) (Fig. 1). The three-dimensional integral in Eq. (5) then reduces to a two-dimensional integral,

\[
\lambda_s = \frac{3\pi e^2}{\pi} \int_0^1 d(kR) \int_0^1 d(\cos \chi) S^L(k, \cos \chi)[j_0^2(kR_1) + j_0^2(kR_2) - 2j_0(kR_1)j_0(kR_2)J_0(kR \sin \chi \sin \theta) \times \cos(kR \cos \chi \cos \theta)],
\]

where \( J_0(x) \) is the zeroth-order Bessel function. The two-dimensional function \( S^L(k, \cos \chi) \) used in Eq. (24) was generated from simulated configurations for the pure fluid of dipolar HSC’s. The results of integration are given as the dependence of \( \lambda_s \) on \( \theta \) for isotropic and nematic solvents (Fig. 10) and as the dependence of \( \lambda_s \) on \( \eta \) at different angles \( \theta \) (Fig. 11).

**Continuum estimate**

A continuum estimate for \( \lambda_s \) can be directly obtained from Eq. (24) by assuming that the response function \( \chi^L(k) \) does not change significantly in the integration range of \( k \) values on which \( |\Delta \tilde{E}^L(k)|^2 \) decays, \( k < 2\pi/R_{1,2} \). This assumption implies that \( \chi^L(k) = \chi^L(0) \) with the following relation for the continuum reorganization energy:

\[
\lambda_s^{\text{cont}} = \frac{1}{3}\lambda_i + \frac{2}{3}\lambda_{\perp} + \lambda_A.
\]

The parallel \( \lambda_i \) and perpendicular \( \lambda_{\perp} \) reorganization components are related to the corresponding projections of the static dielectric constant by the standard Marcus equation:

\[
\lambda_{i,\perp} = \epsilon_{i,\perp} \epsilon_0,
\]

where \( \epsilon_0 \) is the energy of the difference electric field outside the DAC placed in the vacuum.

\[
\epsilon_0 = (8\pi)^{-1} \int |\Delta \tilde{E}^L(k)|^2 \left[dk/(2\pi)^3\right].
\]

For the two-sphere configuration of the DAC, \( \epsilon_0 \) is given by the relation

\[
\epsilon_0 = e^2(1/2R_A + 1/2R_D - 1/R).
\]

In Eq. (26) the Pekar factor

\[
c_{i,\perp} = \epsilon_0^{-1} - \epsilon_{i,\perp}^{-1}
\]

is calculated on a continuous set of \( k \) vectors (lines) and from the continuum estimate (b). The points indicate: \( \theta = 0 \) (squares), \( \theta = 45^\circ \) (diamonds), and \( \theta = 90^\circ \) (circles); \( (m^*)^2 = 1.0 \), \( R_D = R_A = 4 \text{ Å} \), \( R = 10 \text{ Å} \).

**Figure 9.** \( S^L(k, \cos \chi) \) calculated on a continuous set of \( k \) vectors (lines) and from simulations with \( k \) vectors forming the eigenvalues of the cubic simulation box (dots) at \( \eta = 0.438 \). The curves are drawn from \( \chi = 15^\circ \) (upper curve) to \( \chi = 90^\circ \) (lower curve) with the interval 15°.

**Figure 10.** \( \lambda_s \) vs \( \theta \) at packing fractions shown on the plot; \( (m^*)^2 = 1.0 \), \( R_D = R_A = 4 \text{ Å} \), \( R = 10 \text{ Å} \).
TABLE II. Reorganization energy calculated from the longitudinal structure factor \( \lambda_1 \), Eq. (24) and from the continuum estimate \( \lambda_{\text{cont}} \), Eq. (25). The geometric parameters of the donor–acceptor complex are: \( R_D = R_A = 4 \, \text{Å} \) and \( R = 10 \, \text{Å} \).

<table>
<thead>
<tr>
<th>( \eta )</th>
<th>( \theta = 0 )</th>
<th>( \theta = 45^\circ )</th>
<th>( \theta = 90^\circ )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.300</td>
<td>0.25</td>
<td>0.25</td>
<td>0.24</td>
</tr>
<tr>
<td>0.330</td>
<td>0.27</td>
<td>0.27</td>
<td>0.26</td>
</tr>
<tr>
<td>0.360</td>
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<td>0.29</td>
<td>0.28</td>
</tr>
<tr>
<td>0.382</td>
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<td>0.395</td>
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<td>0.30</td>
<td>0.29</td>
</tr>
<tr>
<td>0.407</td>
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<td>0.30</td>
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</tr>
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<tr>
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<td>0.33</td>
<td>0.27</td>
</tr>
<tr>
<td>0.438</td>
<td>0.40</td>
<td>0.33</td>
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</tr>
<tr>
<td>0.457</td>
<td>0.42</td>
<td>0.34</td>
<td>0.27</td>
</tr>
<tr>
<td>0.470</td>
<td>0.42</td>
<td>0.34</td>
<td>0.27</td>
</tr>
</tbody>
</table>

where \( \langle P_2(\cos \theta) \rangle \) reflects the anisotropy of the average orientation of the DAC in the LC solvent. The orientational distribution of the DAC’s can be obtained from time-resolved paramagnetic resonance experiments.\(^{55,56}\) For isotropic orientations, \( \langle P_2(\cos \theta) \rangle = 0 \) and \( \lambda_A = 0 \).

The calculated values of \( \lambda_A \) at different \( \theta \) and \( \eta \) are listed in Table II and are plotted in Figs. 10 and 11. The polarity parameter \((m^+)^2 = 1.0\) corresponds to a low-polarity dipolar fluid (see dielectric constants in Table I) for HSC’s with the aspect ratio 5.0. The reorganization energy \( \lambda_A \) grows approximately linearly with \( \eta \) in this limit, as is seen in Fig. 11 in the isotropic phase where the change in \( \eta \) is caused by the variation of \( \eta \). The linear trend is modified at the transition point: \( \lambda_A \) slopes stronger with \( \eta \) for the parallel orientation \((\theta = 0)\) and drops for the perpendicular orientation \((\theta = 90^\circ)\). This effect is due to a greater ease of the polarization fluctuations in the parallel direction compared to the perpendicular direction, as is seen from the longitudinal structure factor in Figs. 6 and 7(a).

The continuum estimate reproduces the forking of \( \lambda_A \) in the nematic phase due to the anisotropy of the static dielectric constant. It does not, however, take into account a considerable rise of \( \lambda_A \) in the nematic region for all angles \( \theta \), whereas Eq. (24) shows no increase in \( \lambda_A \) with \( \eta \) at \( \theta = 90^\circ \) and a continuing increase at \( \theta = 0 \). The anisotropic dielectric constant therefore does not fully capture the microscopic spectrum of the solvent electrostatic fluctuations in the nematic phase.\(^{18}\) The splitting between the parallel and orthogonal reorganization energies is also much smaller for the continuum model.

V. DISCUSSION

In order to quantify the effect of an anisotropic LC environment on the activation barrier of ET, we consider here a model CS reaction in a two-sphere DAC. The reaction proceeds from a nonpolar state D–A to a polar state D\(^+\)–A\(^-\). The change in the forward and backward activation barriers with the rotation of the DAC relative to the nematic director can be characterized by the reduced rate constants \( \ln(k_{\text{CS}}/k_{\text{CS}}^1) \) and \( \ln(k_{\text{CR}}/k_{\text{CR}}^1) \), where \( k_{\text{CS}}^1 \) and \( k_{\text{CR}}^1 \) refer to the DAC oriented parallel to the nematic director \((\theta = 0, \text{Fig. 1})\). Figure 12 shows the reduced constant for CS (solid lines) and CR (dashed lines) obtained from the Marcus equation (assuming an isotropic pre-exponent)

\[
\ln \frac{k_{\text{CS}}}{k_{\text{CS}}^1} = -\frac{(\hbar \omega_{\text{abs/em}}(\theta))^2}{4k_BT\lambda_x(\theta)} + \frac{(\hbar \omega_{\text{abs/em}})^2}{4k_BT\lambda_x^s},
\]

FIG. 12. \( \ln(k_{\text{CS}}/k_{\text{CS}}^1) \) (solid lines) and \( \ln(k_{\text{CR}}/k_{\text{CR}}^1) \) (dashed lines) vs the angle between the direction of ET and the nematic director. The solid and dashed lines correspond to \( \hbar \omega_{\text{abs}} = 0.6 \, \text{eV} \) (upper curves), 1.0 eV (middle curves), and 1.4 eV (lower curves). The reorganization energy is calculated from simulated longitudinal structure factor at \( \eta = 0.457, R_D = R_A = 4 \, \text{Å}, R = 10 \, \text{Å} \).
where $\omega_{\text{abs}}(\theta)$ and $\omega_{\text{em}}(\theta)$ refer to the average vertical transition energies (first spectral moments). For CS $\omega_{\text{abs}}$ is determined by electronic solvation only and is independent of $\theta$, $\omega_{\text{abs}} \approx \omega_{\text{abs}}$. For CR one gets $\hbar \omega_{\text{em}}(\theta) = \hbar \omega_{\text{abs}} - 2 \lambda_i(\theta)$. From our calculations presented in Fig. 10, $\lambda_i(\theta) - \lambda_i^{\text{sym}} < 0$ and rotations from the parallel alignment ($\parallel$) superscript lead to smaller CS rates (Fig. 12). The result for CR depends on whether the reaction is in the normal or in the inverted region of ET. In the inverted region, the CR rate decays with $\theta$ similarly to the CS rate ($\hbar \omega_{\text{abs}} = 1.0$ and $1.4$ eV in Fig. 12), whereas in the normal region rotations of the DAC from the parallel alignment lead to higher CR rates ($\hbar \omega_{\text{abs}}^{\parallel} = 0.6$ in Fig. 12).

The dependence of the solvent reorganization energy on the orientation of the DAC relative to the nematic director opens the door to exercise an external control over the ET reaction rate. This possibility is based on the separation of the characteristic time scales for microscopic and collective orientational motions. A charge-transfer complex immersed in a LC solvent rotates on a microscopic, nanosecond time scale.\(^{21,55}\) On the other hand, the time scale of director reorientation is of the order of milliseconds to seconds.\(^{58}\) An essentially instantaneous reorientation of the DAC relative to the macroscopic symmetry axis of the solvent by a short polarized laser pulse can practically shut down the CS reaction (Fig. 12). This property may be useful for the molecular switching function.

From the data presented in this study, it is still premature to draw general conclusions about the qualitative change of the solvent reorganization energy in polar LC solvents in the region of IN transition. The reason is that the dipolar strength of $(m_i^+)^2 = 1.0$ used here gives only a weakly polar solvent. The model of HSC’s with longitudinal point dipoles is not very convenient to study the solvent polarity effect since the nematic phase become unstable relative to the smectic-A phase at $(m_i^+)^2 = 6.48$. Solvents with Lennard-Jones interactions, more stable toward variations in the dipolar strength, should be used for an extended analysis of the polarity effect. This study addresses the effect of the change in the orientational order of the solvent on the ET activation barrier. Although this effect is likely the main contribution to the alteration of the ET barrier at the IN transition, the effects of the local-density profile\(^{10}\) and the alteration of the solvent response by the solute excluded volume\(^{39}\) need a separate investigation.

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