Directional energy transfer in columnar liquid crystals: A computer-simulation study

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We have investigated energy transfer between solute molecules in systems of discotic Gay-Berne molecules forming columnar as well as isotropic and nematic mesophases, employing computer experiments that combine Monte Carlo simulations of the phase structure and a stochastic approach to the transfer. The time-dependent excitation probability and the mean square displacement of the initial excitation show an enhanced energy transfer in the columnar phase, with a faster energy transfer along the column axis. [S1063-651X(98)08308-1]

I. INTRODUCTION

Energy transfer (ET) provides a fast and efficient way of transporting excitation energy in condensed phases from an initially excited molecule to one further away [1]. In natural photosynthetic systems a radiationless *dipole-dipole*, or För-ster, type mechanism has been invoked to explain the rapid excitation hopping from one chlorophyll molecule of the light-harvesting antenna system to another until the photo-synthetic reaction center is reached [2,3]. The process takes place over long distances (40–50 Å) and it appears to be a particularly interesting system for transporting excitation energy. Indeed a number of recent works (see, e.g., [4,5]) have proposed rational molecular designs for artificial light harvesting antennas based on building dendrimeric supermolecules [6] or assemblies of multiporphyrin [4] or phtalocyanines [5] pigments in ordered films.

It is therefore not surprising that much interest also exists in finding ways of channeling this transport, which can, in principle, occur over all space, along a certain specific direction.

Columnar discotic mesophases [7] consist of stacks of mesogenic molecules that seem particularly interesting as molecular materials for strongly directional transfer. In an idealized sense they constitute a sort of bundle of molecular wires, with a discotic core surrounded by alkyl chains separating the columns. The columns themselves often have a certain regular structure, for instance, hexagonal in the plane perpendicular to the columns, providing a kind of bundle of would-be molecular wires. It should also be mentioned that there are many possibilities of changing the molecular design of the columns. Indeed, even though columnar systems are a relatively recent acquisition to the liquid-crystal family, there exists an already very large and continuously growing variety of mesogenic cores [8,9], which can also effectively act as host for guest chromophores. Moreover, the radius of the disks and the spacing between the columns can be varied, for instance, by changing the length of the chains normally attached to the cores. Fast photoconduction along the column axis has also been definitely demonstrated by Ringsdorf and co-workers in highly ordered discotics [10].

As far as ET is concerned, pioneering investigations of energy migration in columnar phases have been performed, particularly on hexakis-*n*-alkoxytriphenylene, by Markovitsi and co-workers using steady state and time-resolved lumi-nescence studies on the pure compound [11] and in the presence of perylene energy acceptors [12]. However, a full understanding of ET is intrinsically complicated because the transfer rate depends, as we shall recall later on [13], on the positions and orientations of the molecules exchanging energy. Thus in setting up a modeling procedure for ET in a certain condensed phase a proper accounting of the positional-orientational pair distributions and of their temperature dependence is essential.

In columnar systems it is also important to examine the conditions for having transfer mainly confined within a column (energy guide effect) as opposed to intercolumn hopping (leakage).

We have recently proposed a simple yet powerful method of tackling the ET problem that consists of coupling a computer simulations calculation of equilibrium positions and orientations of all molecules of a certain system and a Markovian simulation of the transfer process [14]. In a first application, we have employed the method to simulate the effect of a phase change from isotropic to nematic and smectic in a system of Gay-Berne rodlike molecules [15] containing a certain concentration of chromophores and we have shown how the ordering and particularly the smectic layering cause changes in the anisotropy of the transfer rate and in the polarization anisotropy of the emitted fluorescence [14]. This Monte Carlo–Markov method seems to be ideally suited to treat the problem of ET in discotic molecular systems that form columnar mesophases, that we have chosen to tackle here.

II. ENERGY TRANSFER

In the Förster type of ET a ''donor'' and an ''acceptor'' molecule are coupled by a dipole-dipole resonance mechanism. The excitation energy is transferred nonradiatively from the originally excited donor with an average rate that can be written as

$$k_{DA}(t) = a \frac{Q_0}{n^4 \tau} \left\langle \frac{\kappa^2(\hat{\mathbf{r}}_{DA}, \mu_D, \mu_A)}{r_{DA}^6} \right\rangle_t \int_0^\infty \frac{f(\tilde{\nu})\epsilon(\tilde{\nu})}{\tilde{\nu}^4} d\tilde{\nu},$$

(1)

where a is a numerical constant [1,13], τ and Q_0 are the lifetime and the quantum yield of the donor in the absence of transfer, n is the scalar refractive index of the medium, r_{DA} is
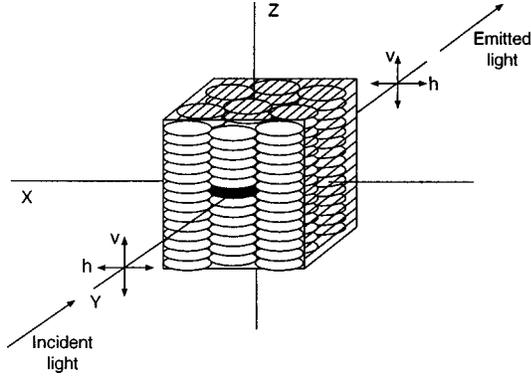
FIG. 1. Experimental geometry considered in the simulations. The exciting plane polarized light parallel (v) or perpendicular (h) to the director (assumed along Z) propagates along the Y axis and impinges on the sample placed at the origin. The emitted fluorescence is observed through a polarizer along the Y axis.

the separation between the two molecules. We shall later use τ as a time scaling factor. The integral is the overlap between $f(\tilde{\nu})$, the fluorescence intensity of the donor and $\epsilon(\tilde{\nu})$ the absorption coefficient of the acceptor in the wave number range $\tilde{\nu}$ to $\tilde{\nu} + d\tilde{\nu}$, normalized so that $\int_0^\infty f(\tilde{\nu}) d\tilde{\nu} = 1$. The anisotropic quantity $\kappa(\hat{\mathbf{r}}_{DA}, \boldsymbol{\mu}_D, \boldsymbol{\mu}_A)$ depends on the unit vectors $\boldsymbol{\mu}_D$, $\boldsymbol{\mu}_A$ defining the orientation of the transition moments for donor and acceptor with respect to the laboratory frame, as well as on the donor-acceptor separation unit vector $\hat{\mathbf{r}}_{DA}$ at time t:

$$\kappa(\hat{\mathbf{r}}_{DA}, \boldsymbol{\mu}_D, \boldsymbol{\mu}_A) = \boldsymbol{\mu}_D \cdot \boldsymbol{\mu}_A - 3(\boldsymbol{\mu}_D \cdot \hat{\mathbf{r}}_{DA})(\boldsymbol{\mu}_A \cdot \hat{\mathbf{r}}_{DA}). \quad (2)$$

The angular brackets in Eq. (1) define a two-particle spatial-orientational-time average over the positions and orientations of particles A and D between the start of excitation (time zero) and a later observation time t. In isotropic systems and when the Förster rate can be isotropically averaged over orientations one has
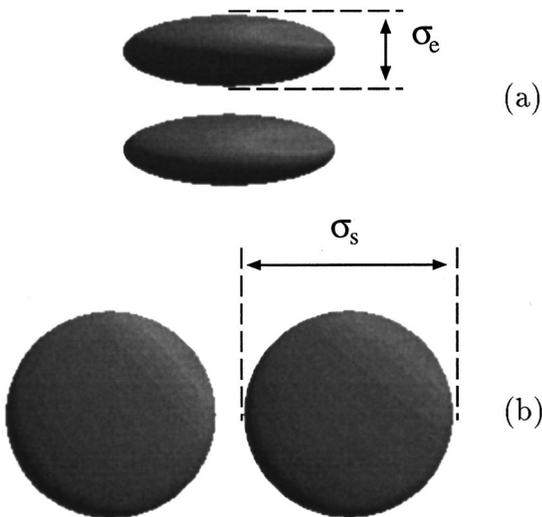

FIG. 2. The *face-to-face* (a) and *side-by-side* (b) configurations for two Gay-Berne disklike particles.

TABLE I. The chosen Gay-Berne state points and the decay times $\langle \tau_{ET} \rangle$ for 128 donors and $R_0 = 1.0\sigma_s$.

T^*	Phase	$\langle P_2 \rangle$ (Ref. [15])	$\langle \tau_{ET} \rangle$
1.0	Columnar	0.992 ± 0.002	0.304 ± 0.002
4.0	Columnar-Nematic	0.903 ± 0.005	0.350 ± 0.004
8.0	Nematic	0.616 ± 0.030	0.355 ± 0.005
20.0	Isotropic	0.048 ± 0.017	0.363 ± 0.007

$$k_{DA} = \frac{1}{\tau} \left(\frac{R_0}{r_{DA}} \right)^6. \quad (3)$$

The "Förster radius" R_0 represents the critical distance at which transfer and radiative decay are equally probable and has the following expression:

$$R_0^6 = a \frac{2Q_0}{3n^4} \int_0^\infty \frac{f(\tilde{\nu})\epsilon(\tilde{\nu})}{\tilde{\nu}^4} d\tilde{\nu}, \quad (4)$$

obtained averaging the orientation factor κ^2 over a random orientational distribution of molecules to get the value $\frac{2}{3}$. It is useful to employ this definition of R_0 as an indication of the spatial range of the transfer also in the more general case of anisotropic media even if the orientational average of κ^2 will then be different from case to case.

The combined average in Eq. (1) is extremely complicated to evaluate and a number of simplifying assumptions are normally made. Since ET is much faster than molecular translation and reorientation, it is often (but with some notable exceptions [16,17]) assumed, as we shall do here, that equilibrium positions and orientations of the molecules are frozen while the transfer process takes place. The assump-
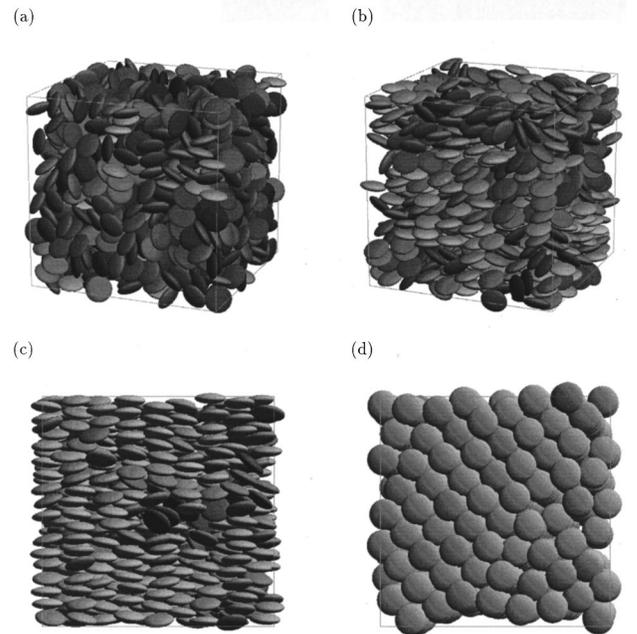

FIG. 3. Snapshots of the Gay-Berne system at the selected temperatures. (a) $T^* = 20.0$ (b) $T^* = 8.0$, (c) $T^* = 4.0$, (d) $T^* = 1.0$. The gray level of each molecule is related to the orientation of the molecular symmetry axis with respect to the director (white if parallel, black if perpendicular).
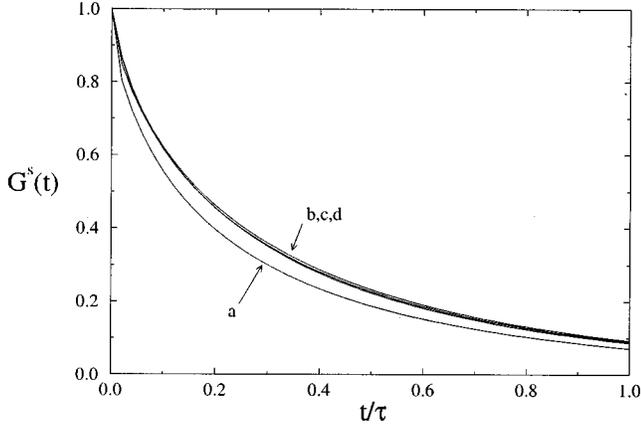
FIG. 4. Excitation Probability G^s for the four examined temperatures; 128 donors, $R_0 = 1.0\sigma_s$. (a) $T^* = 1.0$, (b) $T^* = 4.0$, (c) $T^* = 8.0$, (d) $T^* = 20.0$.

tions mentioned reduce the calculation to a two-particle static average of the dynamic transfer evolution, which, however, is still a major problem, since it requires the pair distribution of the chromophores. The various current theories [18–21] do not allow for correlations between the orientations of the luminescent molecules, a particularly important aspect for anisotropic systems [22] that we wish instead to tackle here.

In previous treatments of ET in columnar systems [11,12] only truly one dimensional (i.e., intracolumnar) processes have normally been treated. An exception is a recent work of Markovitsi and collaborators [23] where, however, a predetermined distribution of centers on a regular lattice was assumed. This clearly prevents the possibility of studying the effect of temperature within a certain phase and of a transition from one phase to a different one.

III. THEORETICAL MODELING

Following our previous treatment [14], we consider ET under the assumption that the fluorescence decay and energy migration take place on a time scale much shorter than that of molecular translations and reorientations, a limit where the viscosity is assumed to be so high or in any case rotation so slow that there is no rotational depolarization of emitted fluorescence.

The incoherent transfer of electronic energy is assumed to be a stochastic Markov process with hopping between N_c states corresponding to the chromophore molecules involved [24–28]. In this description of the process evolution we do not follow the individual excitation jumps from pigment to pigment but we calculate the *probability* $p_i(t)$ of the excitation being on molecule i at time t.

The definition of the master equation that describes the time evolution of $p_i(t)$ and its solution are presented in [14] with the quantities of interest for our study: the excitation decay of the initially excited donor $G^s(t)$, the characteristic decay time $\langle \tau_{\text{ET}} \rangle$ and the fluorescence anisotropy $r(t)$. For the calculation of $r(t)$ we use here a set of equations appropriate to the columnar structure of the system and to the planar location of the transition dipoles that we assume for the discotic molecules. We consider the experimental geometry in Fig. 1 with excitation polarization parallel or perpen-
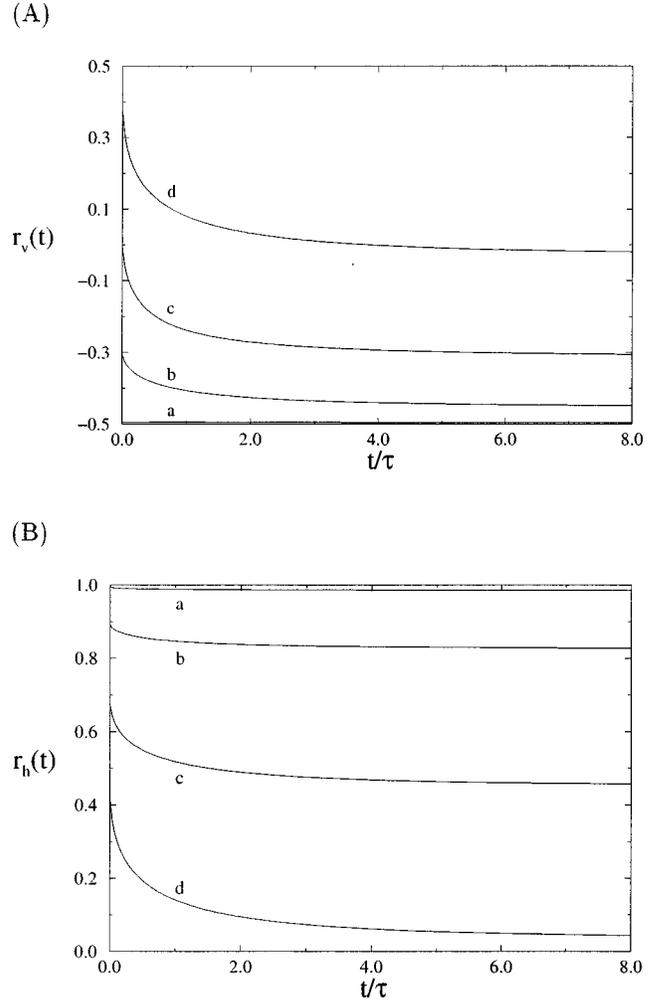

FIG. 5. Polarization Anisotropy for the four examined temperatures; 128 donors, $R_0 = 1.0\sigma_s$. (a) $T^* = 1.0$, (b) $T^* = 4.0$, (c) $T^* = 8.0$, (d) $T^* = 20.0$. (a) $r_v(t)$, vertical excitation; (b) $r_h(t)$, horizontal excitation.

dicular to the director (assumed along Z), i.e., vertical *(v)* or horizontal *(h)* and introduce the respective anisotropy ratios $r_i(t)$,

$$r_v(t) = \frac{I_{ZZ}(t) - I_{ZX}(t)}{I_{ZZ}(t) + 2I_{ZX}(t)}, \tag{5}$$

$$r_h(t) = \frac{I_{XX}(t) - I_{XZ}(t)}{I_{XX}(t) + 2I_{XZ}(t)}. \tag{6}$$

We derive the expressions for the intensities $I_{ii}(t)$ and $I_{ij}(t)$ from the theory of time-dependent fluorescence depolarization in liquid crystals developed in Refs. [14,29,30]. We consider a system of molecules with the symmetry axis of orientations (α_i, β_i), and in practice here we concentrate on disk shape pigments. We can explicitly define the orientation (μ_x, μ_y, μ_z) of the transition dipole, that we consider *perpendicular* to the symmetry axis as

$$\mu_x^{(i)} = \cos \alpha_i \cos \beta_i \cos \gamma_i - \sin \alpha_i \sin \gamma_i \, ,$$

$$\mu_y^{(i)} = \sin \alpha_i \cos \beta_i \cos \gamma_i + \cos \alpha_i \sin \gamma_i \, , \tag{7}$$
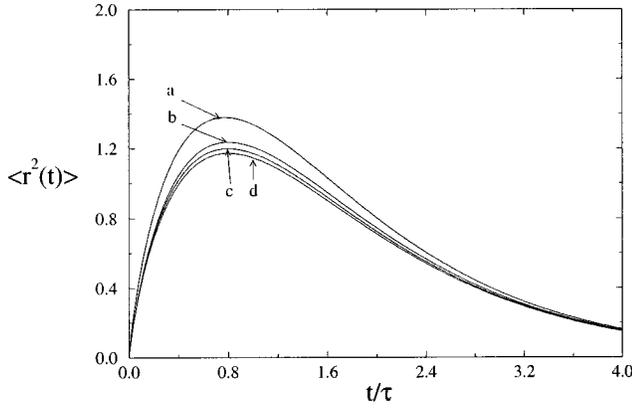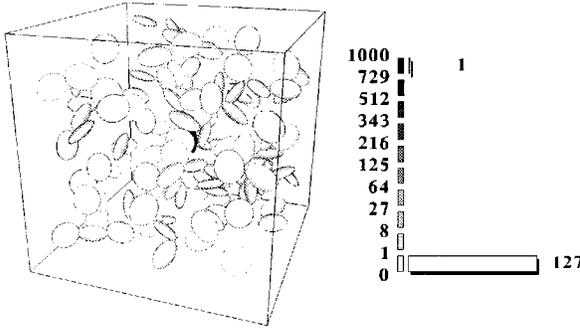
FIG. 6. Mean-square dimensionless displacement $\langle r^2(t)\rangle$ for the four examined temperatures; 128 donors, $R_0=1.0\sigma_s$. (a) $T^*=1.0$, (b) $T^*=4.0$, (c) $T^*=8.0$, (d) $T^*=20.0$.

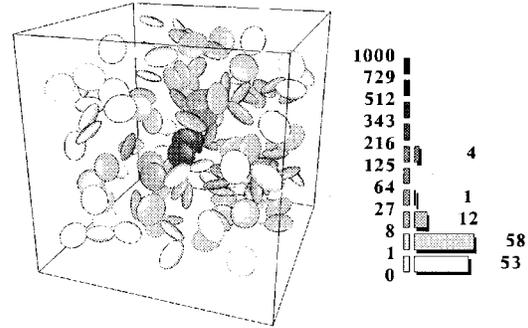$$\boldsymbol{\mu}_z^{(i)}=-\sin\beta_i\cos\gamma_i \, ,$$

where γ_i is the angle of a rotation around the molecular axis. We choose this rotation at random accordingly with the uniaxial symmetry of the molecule. The expressions for the intensities become

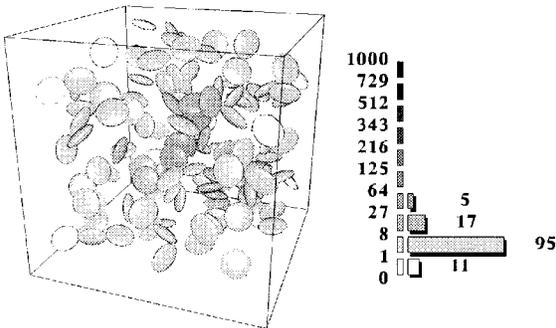$$I_{ZZ}(t)=\left\langle \mu_z^{(i)}(0)^2\sum_{j=1}^{N_c} p_j^i(t)\mu_z^{(j)}(t)^2\right\rangle_{conf} , \qquad (8)$$

$$I_{ZX}(t)=\left\langle \mu_z^{(i)}(0)^2\sum_{j=1}^{N_c} p_j^i(t)\tfrac{1}{2}\left[\mu_x^{(j)}(t)^2+\mu_y^{(j)}(t)^2\right]\right\rangle_{conf} , \qquad (9)$$

$$I_{XX}(t)=\left\langle \tfrac{1}{2}\left[\mu_x^{(i)}(0)^2+\mu_y^{(i)}(0)^2\right] \right.$$
$$\left. \times\sum_{j=1}^{N_c} p_j^i(t)\,\tfrac{1}{2}\left[\mu_x^{(j)}(t)^2+\mu_y^{(j)}(t)^2\right]\right\rangle_{conf} , \qquad (10)$$

$$I_{XZ}(t)=\left\langle \frac{1}{2}\left[\mu_x^{(i)}(0)^2+\mu_y^{(i)}(0)^2\right] \right.$$
$$\left. \times\sum_{j=1}^{N_c} p_j^i(t)\mu_z^{(j)}(t)^2\right\rangle_{conf} , \qquad (11)$$

where $p_j^i(t)$ is the probability for the jth molecule of being excited at time t, after having excited the ith at time 0 in a certain configuration, calculated as in Ref. [14].

Even in a frozen system, where no rotational depolarization exists, the emitted fluorescence radiation will be depolarized by the ET process, as long as the order is not complete. Indeed at very long times, when excitation and emission can be assumed to be uncorrelated, it is possible to obtain the second rank order parameter $\langle P_2\rangle$ from the plateau values $r_i(\infty)$ [29].
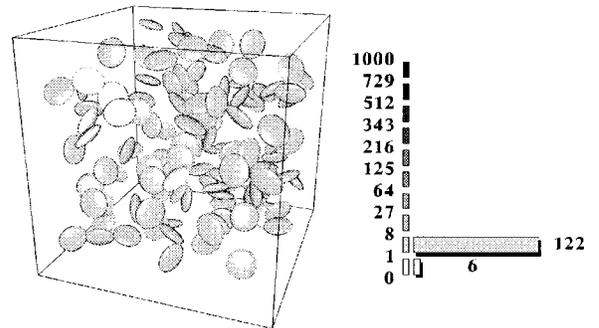

FIG. 7. Three-dimensional representation of the time evolution of the excitation probability for $T^*=20.0$ (isotropic phase), $R_0=1.0\sigma_s$, for different time steps: $t^*=0.00$ (a), $t^*=0.05$ (b), $t^*=0.10$ (c), $t^*=1.0$ (d). The gray level of each molecule is related to its excitation probability according to the palette shown: the histogram and the numbers on the right give the number of molecules with the level of excitation probability (normalized to 10^3) indicated on the left. Only the chromophore system is shown.
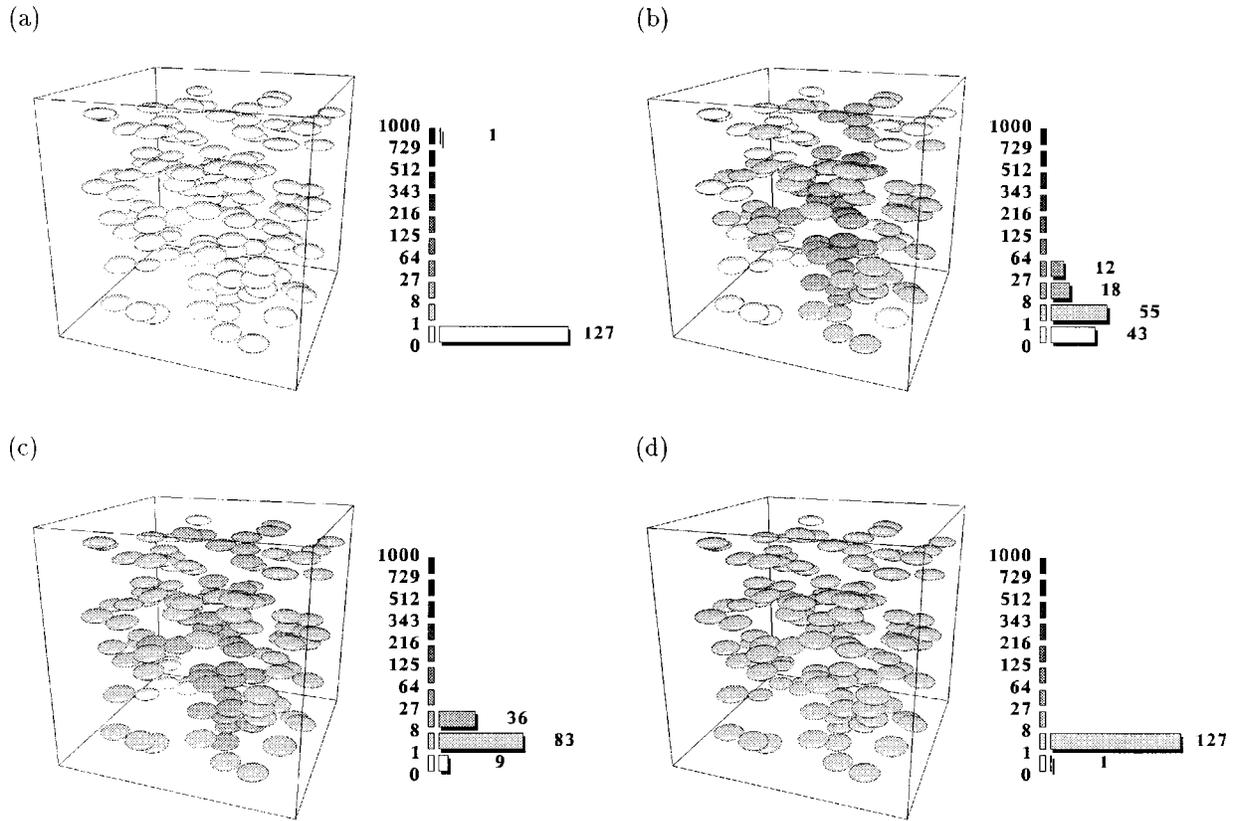
(a)

(b)

(c)

(d)

FIG. 8. Same as Fig. 7 for $T^* = 1.0$ (columnar phase).

$$r_v(\infty) = \frac{-1}{2} \langle P_2 \rangle, \tag{12}$$

$$r_h(\infty) = \frac{\langle P_2 \rangle (6 + \langle P_2 \rangle)}{12 - 5 \langle P_2 \rangle^2}. \tag{13}$$

This is particularly important for structural investigations, because it shows that the orientational order parameter for the pigment can be obtained from a suitable concentration depolarization experiment even when an ordinary rotational depolarization study, based on low concentration measurements, is useless because of the high viscosity of the solvent.

Another quantity that we have found useful to describe the evolution of the ET process is the mean square dimensionless displacement $\langle r^2(t) \rangle$ of the excitation from the initial site defined as

$$\langle r^2(t) \rangle = \left\langle \sum_{j=1}^{N_c} p_j(t) \cdot (r_j/\sigma_s)^2 \right\rangle_{conf}, \tag{14}$$

where $p_j(t)$ represents the excitation probability of the jth molecule placed at a distance r_j from the initially excited one and σ_s is the width of the discotic molecule, here used as unit of length (see next section).

IV. COMPUTER SIMULATIONS

We consider a solute-solvent system formed of disklike ellipsoidal molecules interacting with the Gay-Berne (GB) potential [31], an anisotropic and shifted version of the attractive-repulsive Lennard-Jones 6-12 interaction, where

the strength ϵ and the range parameter σ depend on the orientations of the two particles and on their intermolecular separation vector. σ also depends on molecular parameters such as the width σ_s, and the thickness σ_e of the disk (Fig. 2). The GB potential is particularly interesting for the present work because, by choosing suitable parameters, it can also model columnar mesophases [32]. Its explicit form is

$$U_{GB}^*(\hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j, \mathbf{r}) = 4 \epsilon_s \epsilon(\hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j, \hat{\mathbf{r}})$$

$$\times \left[\left\{ \frac{\sigma_e}{r - \sigma(\hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j, \hat{\mathbf{r}}) + \sigma_e} \right\}^{12} \right.$$

$$\left. - \left\{ \frac{\sigma_e}{r - \sigma(\hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j, \hat{\mathbf{r}}) + \sigma_e} \right\}^6 \right] \tag{15}$$

with unit vectors $\hat{\mathbf{u}}_i$, $\hat{\mathbf{u}}_j$ defining the orientation of the axis of particles i and j; $\mathbf{r} = \mathbf{r}_j - \mathbf{r}_i \equiv r \hat{\mathbf{r}}$ the intermolecular vector of length r. The rather complicated anisotropic contact distance $\sigma(\hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j, \hat{\mathbf{r}})$ and interaction energy $\epsilon(\hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j, \hat{\mathbf{r}})$ are defined as in [31]. We employ a parametrization related to that used by Emerson, Luckhurst, and Whatling in [32] and originally based on the dimensions of a triphenylene core, namely, shape anisotropy $\sigma_e/\sigma_s = 0.345$, interaction anisotropy $\epsilon_e/\epsilon_s = 5$, but using instead energy parameters $\mu = 1$ and $\nu = 3$ as in Ref. [15]. This different choice has the effect of lowering the well depths of the *face-to-face* and *side-by-side* configurations (Fig. 2), thus enhancing the formation of a highly ordered columnar phase [33,34]. More interestingly with this parametrization the array of columns presents an
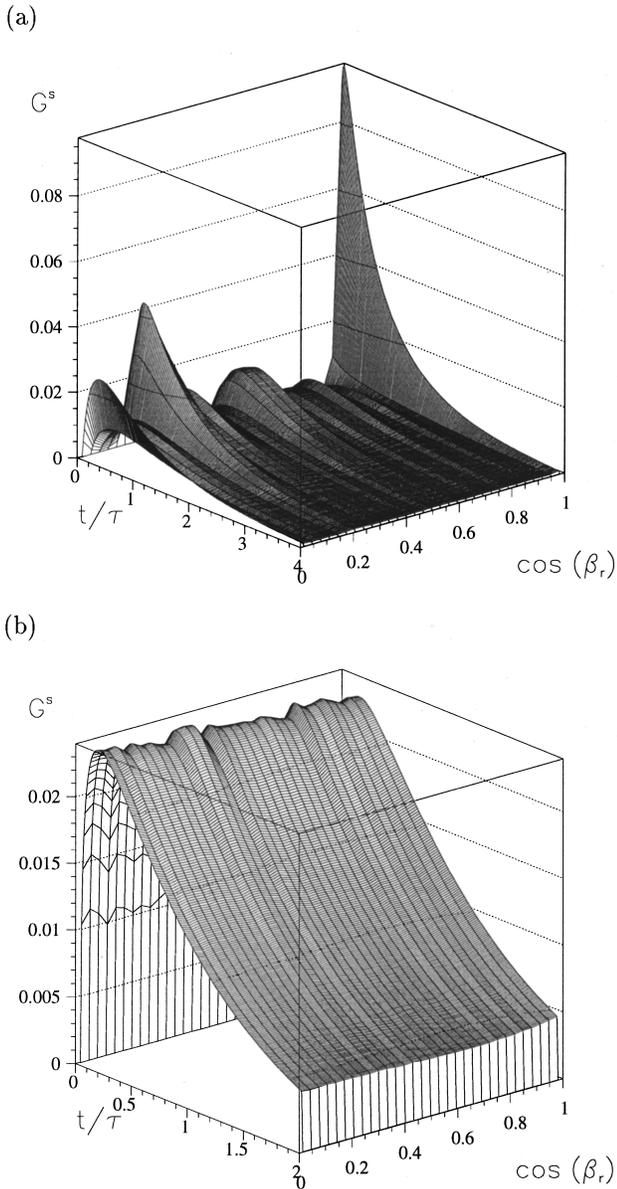
(a)

(b)

FIG. 9. Energy transfer probability density function $G^s(\cos(\beta_r),t)$ for propagation at an angle β_r with respect to the director. Here $R_0 = 1.0\sigma_s$, 128 donors: (a) $T^* = 1.0$ (columnar phase), (b) $T^* = 20.0$ (isotropic phase).

hexagonal structure, as found in various real systems [11,12], rather than a rectangular one as in Ref. [32]. In preparation of the ET study, we have first performed canonical (constant number of particles N, volume V, temperature T) simulations at the same scaled density $\rho^* \equiv N\sigma_s^3/V$: $\rho^* = 2.5$, $N = 10^3$ to approximately locate the phase boundaries. σ_s and ϵ_s are used as molecular units of length and energy. The cutoff radius adopted is $r_c = 1.4\sigma_s$. We have then chosen four scaled temperatures $T^* \equiv kT/\epsilon_s$ corresponding to different phases. In Table I we report the selected temperatures with the type of mesophase obtained and the order parameter $\langle P_2 \rangle$, calculated as in Ref. [15]. In Fig. 3 ''snapshots'' of the molecular configurations corresponding to the selected temperatures are reported. For each temperature 10^4 equilibrium configurations were generated in order to calculate the spectroscopic observables. We assume for simplicity that the

chromophore solutes and the solvent molecules have the same interaction potential. Thus, after the standard Metropolis Monte Carlo (MC) method has been used to generate equilibrium configurations, $N_c = 128$ chromophores are selected at random out of the total of N. The ET process then takes place only among these particles; in order to imitate an infinite system we make use of periodic boundary conditions with the so-called minimum image convention. For this particular chromophore arrangement the $N_c \times N_c$ transition matrix is constructed and diagonalized, next the observables are calculated. The average over the above mentioned 10^4 configurations takes about 2 h on a HP-735 work station using BLAS and LAPACK [35,36] Fast Matrix Multiply and diagonalization routines [35,36].

V. RESULTS AND DISCUSSIONS

In Fig. 4 we plot the decay $G^s(t)$ for the four examined temperatures with range parameter $R_0 = 1.0\sigma_s$ and $N_c = 128$ donors. We can see that there is a faster decay of the initial excitation in the columnar phase (curve a) although the effect is not large. It is interesting to observe that from the isotropic to the highly orientationally ordered phase at $T^* = 4.0$, close to the nematic-columnar transition, the decay results mostly unaffected by the increase of orientational order. We believe that the positional order, due to the columnar arrangements, is responsible for the faster decay observed in the phase at $T^* = 1.0$. This can be observed also in Table I, where we report the calculated characteristic decay times $\langle \tau_{ET} \rangle$. We consider this behavior as a confirmation of the conclusions obtained in our previous work [14].

Particularly important is the effect of phase transformation on the polarization anisotropy. In Fig. 5(a) we display plots for $r_v(t)$ at $R_0 = 1.0\sigma_s$ and 128 donors. This quantity depends strongly from the order and we see a considerable difference between the four cases. It must be stressed that the experimental geometry considered in the calculation of $r_v(t)$ does not appear to be the most appropriate for the highly ordered phases. Indeed, as the order increases, particularly in the columnar phase, a molecule with $\boldsymbol{\mu}$ in the disk plane will absorb less and less radiation when the excitation is vertical. It is therefore useful to consider also the anisotropy $r_h(t)$ obtained from a horizontal excitation. The result for $r_h(t)$ is shown in Fig. 5(b).

In Fig. 6 we show plots of the mean square dimensionless displacement $\langle r^2(t) \rangle$ for the four examined temperatures at $R_0 = 1.0\sigma_s$ and 128 donors. The basic profile of the curves, with a maximum, results from the competition between the spatial evolution of the fluorescence excitation and the fluorescence decay. This quantity gives an indication of the distance that the excitation can reach from the site in which it was originated and as for the $G^s(t)$ it is possible to notice the difference in the behavior of the ET in the columnar phase with respect to the other examined phases.

The change in the evolution process brought about by the formation of the columnar phase is better illustrated in the next two pictures (Figs. 7 and 8). Here we show a three-dimensional representation of the chromophore system and of the time evolution of the excitation transfer for an isotropic and an highly ordered columnar system. For clarity we do not show the whole GB system but only the molecules

involved in the transfer process. The gray level of each molecule is related to its excitation probability according to the palette shown: the histogram and the numbers on the right give the number of molecules that possess a certain level of excitation probability and the value is indicated by the numbers on the left multiplied by 10^3. We see that the propagation of excitation from the initial event is essentially spherical in the isotropic phase (Fig. 7). On the contrary, in the columnar phase (Fig. 8), propagation proceeds mostly along the columns, thus not only with greater speed but also in a nonspherical way.

This can be quantified calculating the probability density for molecules at separation vector direction $\hat{\mathbf{r}}_{ij}$ as a function of the orientation of $\hat{\mathbf{r}}_{ij}$ with respect to the director $\mathbf{n}$, $G^s(\cos(\beta_r),t)$

$$G^s(\cos(\beta_r),t)=\langle \delta(\hat{\mathbf{r}}_{ij}\cdot\mathbf{n}-\cos(\beta_r))p_j^i(t)\rangle_{conf}, \quad (16)$$

where $p_j^i(t)\equiv p(r_{ij},\hat{\mathbf{r}}_{ij},t)$ is the probability for a molecule j, at a separation $\mathbf{r}_{ij}$ from the initially excited molecule i of being excited at time t. The plot of the configuration averaged quantity $G^s(\cos(\beta_r),t)$ at two temperatures in the columnar and isotropic phase (Fig. 9) does indeed support the indication of the snapshots in Figs. 7 and 8 of a strongly anisotropic ET in the ordered mesophase.

VI. CONCLUSIONS

We have examined energy transfer in a liquid crystal that can give columnar phases using a combination of computer simulations of the equilibrium structure of the system with a solution of the master equation for the time evolution of ET that allows full inclusion of positional and orientational order and correlations. We have examined the effects of a phase change, from isotropic, to nematic and columnar, on the qualitative and quantitative features of the ET for a set of chromophores dissolved at a certain concentration. We have found, from the observation of the excitation probability evolving in space (Figs. 7 and 8) that as the system organizes itself in columns, the excitation transfer is more effective along the columns.

The results obtained from our simulations suggest the study of disklike mesogens with increased molecular diameter to thickness ratio. This modification, obtained experimentally e.g., using longer substituents around the mesogenic core of the molecule, should lead to columnar phases with more separation between adjacent columns but the same intracolumnar spacing, thus enhancing the transfer *along* the columns. The control of the shape anisotropy parameter as well as of the coupling radius R_0 may allow the design of a molecular system characterized by larger modifications in the rate and extension of the ET process when it crosses the nematic-columnar phase transition. This in turn could offer interesting possibilities of quasi-one-dimensional transfer in materials that are self-assembling and, being fluid, self-healing.

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