

Energy transfer in condensed systems The effect of phase organization

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Abstract

We investigate the effects that a phase transformation, from isotropic to orientationally (nematic) and positionally (smectic) ordered mesophases, has on the energy transfer process between solute molecules. We combine Metropolis Monte Carlo simulations and a master equation approach to study radiationless energy transfer processes in three-dimensional ordered systems of identical uniaxial particles interacting via the Gay-Berne potential. The time-dependent excitation probability and the fluorescence anisotropy decay curves show an enhanced energy transfer in systems with a higher degree of order. We also find a non-isotropic evolution of the time-dependent excitation probability in systems with positional as well as orientational order, with a faster energy transfer in the smectic planes. © 1997 Elsevier Science B.V.

1. Introduction

The transfer of energy from an excited molecule to other molecules of the same or of different type in a fluid solution is an extremely important process that has been studied for more than half a century, when Förster proposed his mechanism for the radiationless transfer of electronic energy between molecules [1,2]. One of the most important manifestations of the effect is in the rapid energy migration from one chlorophyll (Chl) molecule to another, that follows the primary excitation in a photosynthetic unit. In the antenna system, constituted by a few hundred Chl molecules [3], embedded in the thylakoid membrane and at relatively large distances, because of interspersed lipids [4], this process seems to allow the excitation to reach the actual reaction site, where the energy is employed in the photosynthetic process. In the dipole-dipole resonance mechanism, proposed by Förster, excitation energy is transferred non-radiatively from a “donor” to

an “acceptor” molecule with an average rate that can be written as

$$k_{\text{DA}}(t) = a \frac{Q_0}{n^4 \tau} \left\langle \frac{\kappa^2(\hat{r}_{\text{DA}}, \boldsymbol{\mu}_{\text{D}}, \boldsymbol{\mu}_{\text{A}})}{r_{\text{DA}}^6} \right\rangle_t \times \int_0^\infty \frac{f(\tilde{\nu}) \epsilon(\tilde{\nu})}{\tilde{\nu}^4} d\tilde{\nu}, \quad (1)$$

where a is a numerical constant [1,2], 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 and r_{DA} is the separation between the two molecules. The integral is the overlap between $f(\tilde{\nu})$, the fluorescence intensity of the donor and $\epsilon(\tilde{\nu})$ is the absorption coefficient of the acceptor in the wavenumber 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 $\kappa(\hat{r}_{\text{DA}}, \boldsymbol{\mu}_{\text{D}}, \boldsymbol{\mu}_{\text{A}})$ depends on the unit vectors $\boldsymbol{\mu}_{\text{D}}$, $\boldsymbol{\mu}_{\text{A}}$ defining the orientation of the transition moments for

the donor and acceptor with respect to the laboratory frame, as well as on the donor–acceptor separation unit vector \hat{r}_{DA} at time t :

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

The parentheses in Eq. (1) define a space-time average over the positions and orientations of particles A and D between the excitation (time zero) and a later observation time t . This combined two-particle spatial orientational time average is extremely complicated to evaluate in full generality and a number of simplifying assumptions are normally made. The first considers the centres of mass to be fixed on the experimental timescale, since energy transfer is much faster than molecular translation, and thus only deals with the effect of the molecular reorientation dynamics. Even with this assumption only the two limiting situations with molecular reorientations occurring either rapidly (asymptotic limit) or hardly at all (frozen limit) on the energy transfer timescales are normally considered, even if there are some exceptions [5,6]. The assumptions mentioned reduce the calculation to a two-particle static average of the dynamic transfer evolution. For instance, in their successful GAF theory [7], Fayer and co-workers treat the case of a pure donor system with a certain concentration and uniform distribution of molecular positions and orientations and deal with the Förster rate isotropically averaged over orientations:

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

The “Förster radius” R_0 represents the critical transfer 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 $\frac{2}{3}$. We shall find it useful to use this definition of R_0 as an indication of the range of the transfer also in the more general case of anisotropic media even if the orientational average of κ^2 will then be taken separately. The various current theories [7,9–15] do not

allow for correlations between the orientations of the luminescent molecules [8], an important aspect that we wish to tackle here. Even more important, most approaches deal with disordered systems while less has been done for systems with positional and/or orientational order. On the other hand, even beyond liquid crystal systems, there are many interesting situations in which the orientational dependence of the transfer rate cannot be neglected. For example in various natural photosystems the orientation of the pigment molecules is not random but rather it is determined by the order in a bilayer membrane structure, possibly so as to maximize the harvesting of solar energy [17–19].

Here we wish to investigate the effect of the molecular ordering and examine how it influences the transfer. The major difference with ordinary isotropic systems is thus in the different molecular organization, while the spectral part is essentially the same. We consider energy transfer under the assumption that the fluorescence decay and energy migration take place on a timescale much shorter than that of molecular translations and reorientations, a limit where the viscosity is assumed to be so high or the rotation so slow that there is no rotational depolarization of emitted fluorescence. The intermediate case, where the rotational correlation time is of the same order of magnitude as the inverse of the transfer rate is not considered here, but will be the subject of a subsequent paper [20].

2. Energy transfer

The incoherent transfer of electronic energy is assumed to be a stochastic Markov process with continuous evolution between N_c states where N_c is the number of the chromophore molecules involved [12–16]. In this description of the process evolution we do not follow the individual excitation jumps from chromophore to chromophore, but we calculate the probability $p_i(t)$ of the excitation being on molecule i at time t . This quantity is given by the following master equation:

$$\frac{dp_i(t)}{dt} = \sum_{j=1}^{N_c} \Pi_{ij} p_j(t), \quad (i = 1, 2, \dots, N_c), \quad (5)$$

where the vector \mathbf{p} contains the excitation probability for each of the N_c molecules. The stochastic matrix $\mathbf{\Pi}$ is defined as follows:

$$\Pi_{ij} = \begin{cases} k_{ij}, & i \neq j, \\ -\sum_{\substack{l=1 \\ l \neq i}}^{N_c} k_{il} - \frac{1}{\tau}, & i = j \end{cases} \quad (6)$$

and depends on the configuration of the system, i.e. the position and orientation of all the molecules. The off-diagonal elements $k_{ij}(\hat{\mathbf{r}}_{ij}, \boldsymbol{\mu}_i, \boldsymbol{\mu}_j)$ represent the energy transfer rate between molecules i and j according to the Förster mechanism:

$$k_{ij}(\mathbf{r}_{ij}, \boldsymbol{\mu}_i, \boldsymbol{\mu}_j) = \frac{3}{2} \frac{\kappa^2(\hat{\mathbf{r}}_{ij}, \boldsymbol{\mu}_i, \boldsymbol{\mu}_j)}{\tau} \left(\frac{R_0}{r_{ij}} \right)^6. \quad (7)$$

Eq. (5) has the following formal solution:

$$\mathbf{p}(t) = \exp(t\mathbf{\Pi}) \mathbf{p}(0). \quad (8)$$

This matrix exponential is obtained by numerical diagonalization of the real symmetric matrix $\mathbf{\Pi}$ and the excitation probability can then be expressed as a sum of exponentials

$$p_i(t) = \left\langle \sum_{jk} X_{ij} e^{\lambda_j t} X_{kj} p_k(0) \right\rangle_{\text{conf}}. \quad (9)$$

where \mathbf{X} is the matrix of eigenvectors, λ_i are the eigenvalues and the vector $\mathbf{p}(0)$ represents the initial conditions of the system. In our case we consider that only the i th donor is excited at time zero, thus the vector contains all null elements except the i th which will be one: $p_k(0) = \delta_{i,0}$. An alternative to solving the evolution equation by diagonalization is a sampling method that follows the excitation in the system as it jumps from donor to donor [12]. The ensemble average is obtained by repeating the diagonalization procedure for a number of configurations high enough to give sufficiently good statistics. Even with this numerical approach to the excitation dynamics the problem of donor–acceptor space distribution has still to be tackled. The simplest, albeit drastic, approximation has been to neglect pair correlation and generate random molecular positions in a finite volume, or to fix them on a lattice, and generate orientations at random [13–16] in the static limit. With the advent of Monte Carlo (MC) and molecular dynamics

Table 1

The chosen Gay–Berne state points and the decay times $\langle\tau_{\text{ET}}\rangle = Q/\tau$ for 128 donors and $R_0 = 3.0$

T^*	Phase	$\langle P_2 \rangle$ [23]	$\langle\tau_{\text{ET}}\rangle$
1.6	high-order smectic	0.960 ± 0.002	0.0574 ± 0.0003
2.2	smectic	0.901 ± 0.005	0.0653 ± 0.0008
3.4	nematic	0.634 ± 0.028	0.0782 ± 0.0011
4.0	isotropic	0.089 ± 0.035	0.0836 ± 0.0014

(MD) computer simulations, the possibility of using pair correlations obtained from simulations has started to be exploited [21]. Here we propose a different strategy, where MC simulations of molecular organization and the stochastic simulation of energy transfer are more strictly integrated and rather than going through pair correlations equilibrium configurations, the sets of equilibrium positions and orientations of molecules, generated by the simulations, are directly employed to perform the average in Eq. (9). This is particularly helpful in this work, where we wish to investigate the effect of a phase transformation on the energy transfer process.

3. Computer simulations

We study a solute–solvent system of elongated ellipsoidal molecules interacting with the Gay–Berne (GB) potential [22,23], an anisotropic and shifted version of the 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 vector. σ also depends on molecular parameters such as the length σ_e and breadth σ_s . The GB potential is particularly interesting because, by choosing suitable parameters, it can model not only isotropic phases, but the most important mesophases such as nematic and smectic A and B [23]. We use the same definition and parametrization of the Gay–Berne potential described in Ref. [23] and perform canonical (constant N, V, T) simulations with the same scaled density $\rho^* \equiv N\sigma_s^3/V$: $\rho^* = 0.3$. We choose 4 scaled temperatures $T^* \equiv kT/\epsilon_0$ corresponding to different phases. In Table 1 we report the selected temperatures with the type of mesophase and the order parameter $\langle P_2 \rangle$, calculated as in Ref. [23]. We have studied systems of $N = 10^3$ molecules for each tem-

perature and for each one 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 MC method has been used to generate equilibrium configurations, a random sampling is employed to choose $N_c = 128$ chromophores out of the total of N . The energy transfer 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 workstation using BLAS and LAPACK [26,27] fast matrix multiply and diagonalization routines [26,27]. For most of the calculations we have used a value of the Förster radius of $R_0 = 3.0\sigma_s$. We have then varied this parameter as well as the number of chromophores in separate calculations in order to observe the effect of increasing the range of the transfer process and the chromophore concentration. Once the excitation probability is known from Eq. (9) we can calculate the quantities of interest: the excitation decay of the initially excited donor $G^s(t)$, the quantum yield Q and the fluorescence anisotropy $r(t)$, which we now describe. If we indicate by $p_j^i(t)$ the probability for the j th molecule of being excited at time t , after having excited the i th at time 0, we have, for the initially excited molecule

$$G^s(t) = \langle p_i^i(t) \rangle_{\text{conf}}. \quad (10)$$

The experimentally measurable quantum yield Q , written as

$$Q = \int_0^{\infty} G^s(t) dt / \tau \quad (11)$$

can be used as a measure of the rate of the global energy transfer process. It is also useful to consider polarized fluorescence experiments where plane polarized light with a polarization e_{in} is used for the excitation and the fluorescence emission is observed through an analyzer at e_{out} . The intensity emitted from chromophore j after a time t from the excitation of molecule i will be

$$I_{\text{in,out}}^{(ij)}(t) \propto [e_{\text{in}} \cdot \mu^{(i)}(0)]^2 \times [e_{\text{out}} \cdot \mu^{(j)}(t)]^2 p_j^i(t). \quad (12)$$

The observed intensity is obtained summing over all possible emitters j and taking a configurational average over the absorber i . We consider here the standard vertical (I_{\parallel}) or horizontal (I_{\perp}) polarizer setting and introduce an anisotropy ratio $r(t)$ as

$$r(t) = \frac{I_{\parallel}(t) - I_{\perp}(t)}{I_{\parallel}(t) + 2I_{\perp}(t)}. \quad (13)$$

We derive expressions for $I_{\parallel}(t)$ and $I_{\perp}(t)$ from the theory of time-dependent fluorescence depolarization in liquid crystals developed in Refs. [24,25]. For a system of molecules with transition dipole parallel to the symmetry axis and orientations (α_i, β_i)

$$I_{\parallel}(t) \propto \left\langle \cos^2 \beta_i \sum_{j=1}^{N_c} p_j^i(t) \cos^2 \beta_j(t) \right\rangle_{\text{conf}}, \quad (14)$$

$$I_{\perp}(t) \propto \left\langle \cos^2 \beta_i \sum_{j=1}^{N_c} p_j^i(t) \sin^2 \beta_j(t) \cos^2 \alpha_j(t) \right\rangle_{\text{conf}}. \quad (15)$$

Notice that even in a frozen system, where no rotational depolarization exists, the radiation will be depolarized by the energy transfer process, as long as the order is not complete. Indeed at long times, where excitation and emission can be assumed to be uncorrelated, we expect $r(\infty) = \langle P_2 \rangle$. This is particularly important, because it shows that the order parameter 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.

4. Results and discussions

In Fig. 1 (A) we plot the decay $G^s(t)$ for the 4 examined temperatures with range parameter $R_0 = 3.0$ and $N_c = 128$ donors. We can see that there is a slightly faster decay of the initial excitation in systems with higher order. This can also be observed in Table 1, where we report the calculated characteristic decay

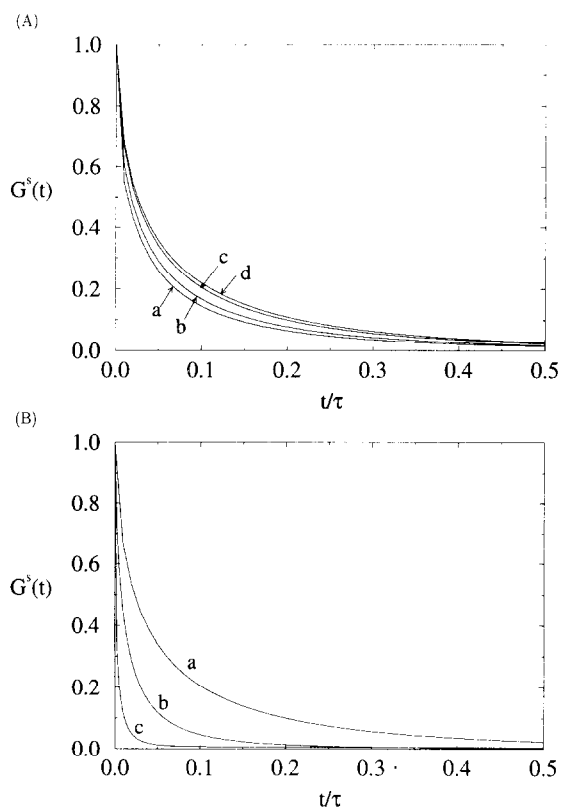


Fig. 1. (A) Excitation probability G^s for the 4 examined temperatures; 128 donors, $R_0 = 3.0$. (a) $T^* = 1.6$, (b) $T^* = 2.2$, (c) $T^* = 3.4$, (d) $T^* = 4.0$. (B) Excitation probability G^s for $T^* = 3.4$. (a) $R_0 = 3.0$, 128 donors; (b) $R_0 = 3.0$, 256 donors; (c) $R_0 = 5.0$, 128 donors.

Table 2
Decay times for $T^* = 3.4$ with $R_0 = 5.0$ or 256 donors

T^*	R_0	N_c	$\langle\tau_{ET}\rangle$
3.4	3.0	128	0.0782 ± 0.0011
3.4	3.0	256	0.0259 ± 0.0001
3.4	5.0	128	0.0118 ± 0.0003

times $\langle\tau_{ET}\rangle = \int_0^\infty G^s(t) dt$. In Fig. 1 (B) the G^s relative to the nematic temperature $T^* = 3.4$ is compared with two analogous calculations in which $R_0 = 5.0$ and the number of chromophores is increased to 256. As we may expect the decay is much faster. In particular we see that the value of the Förster radius can dramatically affect the global rate of the transfer process. In Table 2 the corresponding characteristic decay

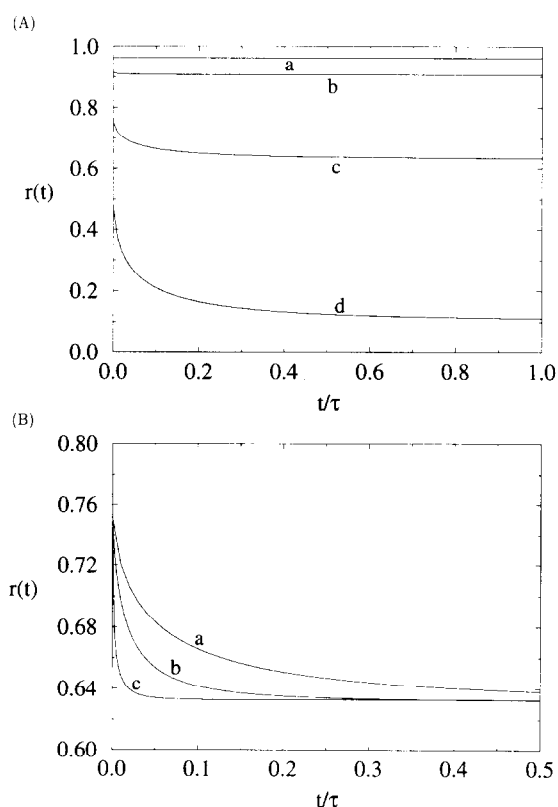


Fig. 2. (A) Polarization anisotropy $r(t)$ for the 4 examined temperatures; 128 donors, $R_0 = 3.0$. (a) $T^* = 1.6$, (b) $T^* = 2.2$, (c) $T^* = 3.4$, (d) $T^* = 4.0$. (B) Polarization anisotropy $r(t)$ for $T^* = 3.4$. (a) $R_0 = 3.0$, 128 donors; (b) $R_0 = 3.0$, 256 donors; (c) $R_0 = 5.0$, 128 donors.

times are reported. Particularly important is the effect of phase transformation on the polarization anisotropy $r(t)$. In Fig. 2 (A) we display plots for $r(t)$ at $R_0 = 3.0$ and 128 donors. This quantity depends strongly on the order and we see a considerable difference between the four cases. In particular, the plateau value of the curves gives the $\langle P_2 \rangle$ order parameters, as expected. In Fig. 2 (B) we show the effect of increasing the Förster radius to $R_0 = 5.0$ and N_c to 256 and we see the profound effect it has on the dynamics.

The change in the evolution process brought about by the formation of the liquid crystal phase is better illustrated in the next two pictures (Figs. 3 and 4). 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

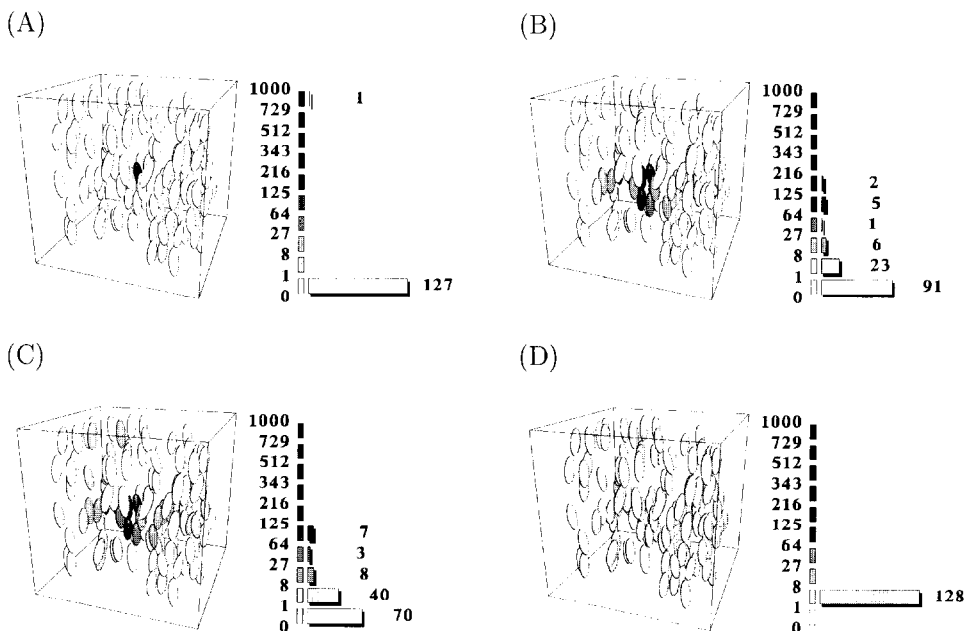


Fig. 3. Three-dimensional representation of the time evolution of the excitation probability for $T^* = 1.6$ (smectic phase) at time $t^* = 0.00$ (A), $t^* = 0.05$ (B), $t^* = 0.10$ (C), $t^* = 1.0$ (D). The gray level of each molecule is related to its excitation probability according to the palette 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.

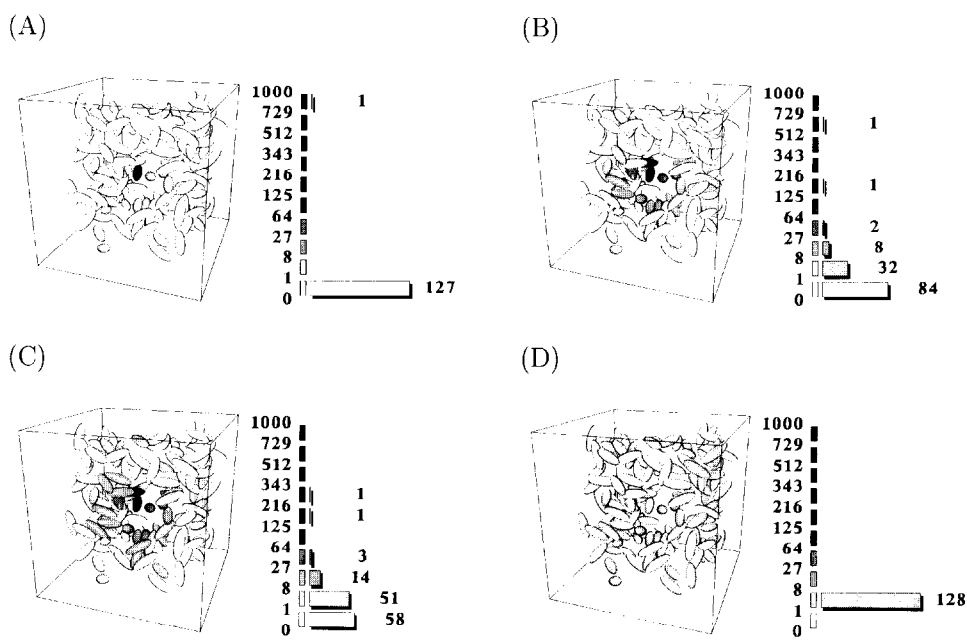
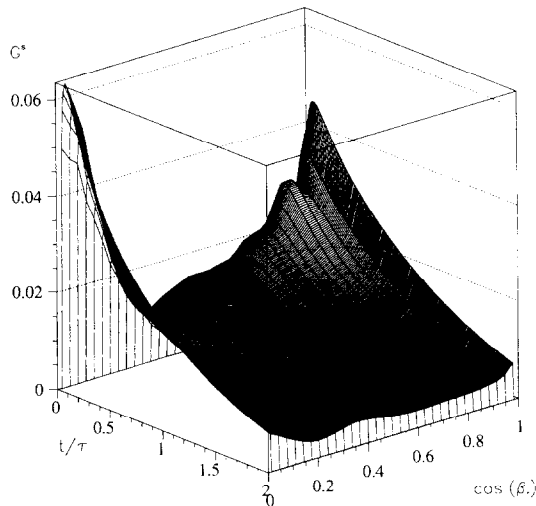


Fig. 4. Same as Fig. 3 for $T^* = 4.0$ (isotropic phase)

(A)



(B)

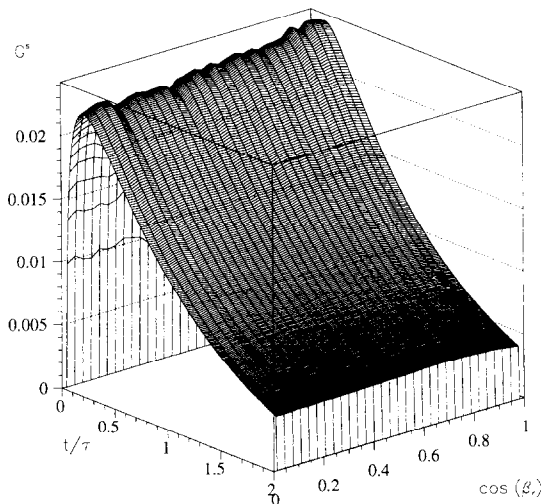


Fig. 5. Energy transfer probability density function $G^s(\cos(\beta_r), t)$ for propagation at an angle β_r with respect to the director. Here $R_0 = 3.0$, $N_c = 128$ donors: (A) $T^* = 1.6$ (smectic phase), (B) $T^* = 4.0$ (isotropic phase).

ordered smectic 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 expressed in thousands. We see that the propagation of excitation from the initial event is essentially spherical in the isotropic phase. On the contrary, in the smectic phase the propagation proceeds through the layers, not only with greater speed but also in a non-spherical way. This can be quantified calculating the probability density for molecules in the separation vector direction \hat{r}_{ij} as a function of the orientation of \hat{r}_{ij} with respect to the director \mathbf{n} , $G^s(\cos(\beta_r), t)$

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

where $p_j^i(t) \equiv p(r_{ij}, \hat{r}_{ij}, t)$ is the probability for a molecule j , at a separation 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 smectic and isotropic phase (Fig. 5) does indeed support the indication of the snapshots in Figs. 3, 4 of a strongly anisotropic energy transfer in the ordered mesophase.

5. Conclusions

In this Letter we have described a simple and fairly general method of coupling the computer simulation of the equilibrium structure of a fluid and the solution of the master equation for the time evolution of energy transfer. This allows the full inclusion of positional and orientational order and correlations and can be easily applied to the modeling of a variety of systems even in the presence of quenchers or statistical traps. Here we have examined the effects of a phase change, from isotropic, to nematic and smectic, on the qualitative and quantitative features of the energy transfer for a set of chromophores dissolved at a certain concentration. We find that the orientational dependence of the radiationless energy transfer process has only a slight direct influence on the decay

rate. The main factor in determining the transfer rate seems to be the molecular separation, and thus the positional organization, through the term at the sixth inverse power of distance (cf. Eq. (7)). However, the onset of ordering allows the molecules to come closer and enhances the transfer. Also an increase in concentration, effectively reducing the average distances between molecules, or an increase in the Förster radius leads to a dramatic change in the global transfer rate. The results obtained for the polarization anisotropy $r(t)$ show that it is possible to study the orientational order via energy transfer-concentration depolarization experiments in high-viscosity systems, such as liquid crystal polymers, where rotational depolarization does not take place. We have also found, from the observation of the excitation probability evolving in space (Figs. 3 and 4) that in systems with positional order the excitation follows a preferential evolution pattern and that the transfer seems to be more effective in the smectic planes. We think that this new positional aspect, together with its coupling to orientational order, should be of particular interest in the molecular design of effective light harvesting devices.

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