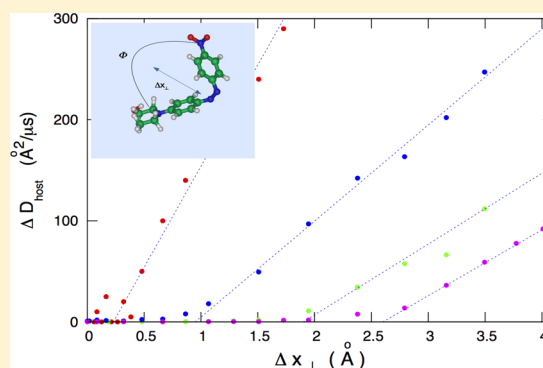


Stimuli Thresholds for Isomerization-Induced Molecular Motions in Azobenzene-Containing Materials

V. Teboul*

Laboratoire de Photonique d'Angers EA 4464, Université d'Angers, Physics Department, 2 Bd Lavoisier, 49045 Angers, France

ABSTRACT: We use large-scale molecular dynamics simulations of the isomerizations of azobenzene molecules diluted inside a simple molecular material to investigate the effect of a modification of the cis isomer shape on the induced diffusion mechanism. To this end we simulate incomplete isomerizations, modifying the amplitude of the trans-to-cis isomerization. We find thresholds in the evolution of the host molecules mobility with the isomerization amplitude, a result predicted by the cage-breaking mechanism hypothesis (Teboul, V.; Saiddine, M.; Nunzi, J. M.; Accary, J. B. *J. Chem. Phys.* **2011**, *134*, 114517) and by the gradient pressure mechanism theory (Barrett, C. J.; Rochon, P. L.; Natansohn, A. L. *J. Chem. Phys.* **1998**, *109*, 1505–1516.). Above the threshold the diffusion then increases linearly with the variation of the chromophore size induced by the isomerization.



I. INTRODUCTION

Under the nanoscale stimuli induced by the isomerization of diluted azo-dyes, soft matter undergoes intriguingly large macroscopic transport phenomena.¹ The subject has attracted a large number of investigations due to the various possible applications ranging from biological applications^{2–4} to the information storage^{5–7} and nanotechnology.^{8–15} This unexplained isomerization-induced transport is also of fundamental interest due to a possible connection^{16,17} with the glass-transition long-standing problem.^{18–21} If that transport property is without any doubt due to the photoisomerization of the dyes, the physical mechanisms that lead to that transport are still the object of conjectures. Various mechanisms have been proposed¹ to explain that transport. The proposed mechanisms include the mean field induced by the dipolar attraction between the azo dyes,^{22,23} the incident light electric field gradient,²⁴ the mechanical stress induced by the orientation of the dyes,²⁵ the pressure gradients induced inside the material by the isomerizations,^{26,27} an isomerization-induced cage breaking process around the azo-dyes,¹⁷ then followed (or not) by the modification of spontaneous cooperative mechanisms in soft matter,^{16,20} the periodic modification of the free-volume^{28,29} around the dye induced by the isomerization, and the reptation of the dye along the polarization direction.³⁰ To complicate somehow these pictures, we expect different physical mechanisms to appear sequentially during the surface relief grating (SRG) formation.^{1,31} For short time scales the chromophore's isomerization induces molecular rearrangements around the chromophore that lead to the motion of surrounding host molecules^{16,17,26,27,30} and eventually to its own motion, resulting in the rotation of the chromophore even at low temperatures when the thermal diffusion is small. Then, because of the preferential light absorption in the chromophore's dipole direction, the

chromophores align themselves along a direction perpendicular to the electric field of the incident light,^{1,30} leading to the appearance of new physical mechanisms.^{22–25} Recent experiments³¹ show that the two different physical mechanisms (dipole-induced or isomerization-induced) also cohabit for larger time scales, a result that one expects as long as there are still isomerizations in the medium. In this work we are interested only in the short-time physical mechanisms that are directly induced by the isomerizations. Note, however, that the effect of the alignment has already been studied extensively.^{1,22–25}

Molecular dynamics (MD) simulations^{32,33} is an invaluable tool to unravel condensed matter physics phenomena^{34–38} at the microscopic level. To shed some light on the physical mechanism at the origin of the induced transport, in this paper we use MD simulations to investigate the effect of a modification of the stimuli. For that purpose we “artificially” tune in the simulations the amplitude of the chromophore isomerization (Figure 1a,b), and then study the response generated by the corresponding variation of the isomerization-induced stimuli on the diffusion process. Our aim is to search for the existence of stimuli thresholds for the isomerization-induced diffusion. In the cage-breaking picture,¹⁷ during the isomerization process, the chromophore pushes a few nearby host molecules out of their cages, inducing diffusion. For that process to occur, the change of shape of the chromophore has to be large enough to push host molecules through their caging potential barrier into a new minimum of the mean field potential. As a result, in the cage breaking picture there is an isomerization amplitude threshold to induce diffusion. The

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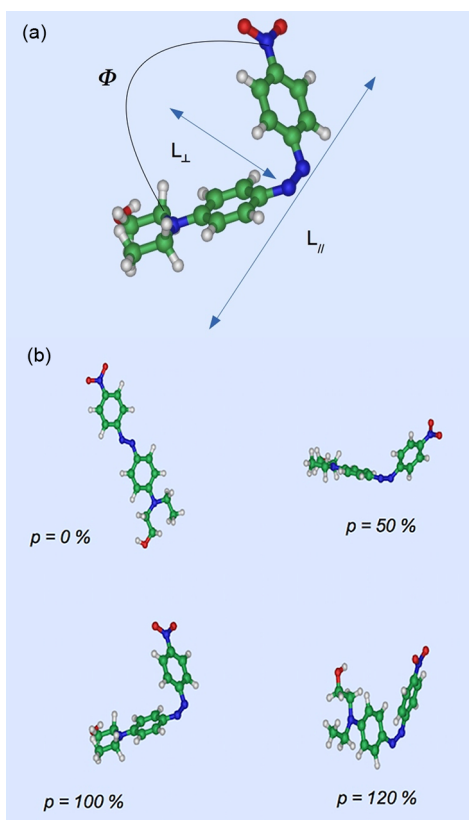


Figure 1. (a) Opening angle, ϕ , length, $L_{||}$ and width, L_{\perp} , of the chromophore. We define $\theta = \pi - \phi$ and $p = \theta/\theta_0$, where θ_0 corresponds to the true *cis*-DR1 isomer. The picture shows the particular *cis* isomer ($p = 100\%$, $\theta = \theta_0$, $\phi = \phi_0$), but the resulting definitions of θ , $L_{||}$, and L_{\perp} are intended to be applied for any configuration (i.e., any p value). From these lengths, we define $\Delta x_{||} = L_{||}^{\text{trans}} - L_{||}$ and $\Delta x_{\perp} = L_{\perp} - L_{\perp}^{\text{trans}} \approx L_{\perp}$. (b) DR1 chromophore molecule displayed with various amplitudes of isomerizations. We define the angle $\theta = \pi - \phi$, where ϕ is the opening angle of the DR1 isomer in the *cis* configuration. $p = \theta/\theta_0$, where θ_0 is the angle of the true *cis*-DR1 isomer.

other theory that predicts thresholds is the pressure gradient theory.^{26,27} In this theory the molecular motions are induced by the pressure gradient created on the medium by the change of the effective volume of the chromophore during its isomerization. The pressure gradient, in that theory, thus has to overpass the material stress threshold to permit the molecular motions. In addition to the theoretical interest for the explanation of the physical mechanism, the existence of thresholds implies minimal conditions on the stimuli to induce the motions. More generally, we expect a study of the *cis* isomer shape dependence on the diffusion process to lead to optimization parameters for the SRG processes and the related applications.^{2–11}

II. CALCULATIONS

We simulate the photoisomerization of one ($N_c = 1$) “dispersed red one” (DR1) molecule ($C_{16}H_{18}N_4O_3$, the probe) inside a matrix of $N = 2688, 800$, or 300 linear molecules (the host). We use periodic boundary conditions. At constant density, ρ , a decrease in the number, N , of host molecules corresponds to a decrease in the simulation box volume, v , as N_c is constant. For our smaller N value ($N = 300$), we found that size effects increase slightly the viscosity of the host but the resulting

modifications of the dynamics in the vicinity ($R < 10 \text{ \AA}$) of the chromophore are within the error margins of our results. Consequently, we find a linear increase in the induced diffusion with the chromophore’s concentration. A detailed description of the simulation procedure can be found in previous works.^{39,40} The main difference is that, taking into account the universality of the effect,¹ in this article we simplify the host molecules as much as possible to better understand the effects of the isomerization on the medium. We found that simulations using methyl methacrylate host molecules,⁴¹ as in refs 39 and 40, lead to similar threshold effects to the ones we report in this study, but we simplified the host to reach larger time scales and decrease the uncertainties of our results. We model the host molecules as constituted of two atoms ($i = 1, 2$) that do interact with the following Lennard–Jones potentials: $V_{ij} = 4\epsilon_{ij}((\sigma_{ij}/r)^{12} - (\sigma_{ij}/r)^6)$ with the parameters: $\epsilon_{11} = \epsilon_{12} = 0.5 \text{ kJ/mol}$, $\epsilon_{22} = 0.4 \text{ kJ/mol}$, $\sigma_{11} = \sigma_{12} = 3.45 \text{ \AA}$, and $\sigma_{22} = 3.28 \text{ \AA}$. We use the mass of argon for each atom of the linear host molecule that we rigidly bonded fixing the interatomic distance to $d = 1.73 \text{ \AA}$. With these parameters the host (alone or mixed with the probe) does not crystallize, even during long simulation runs. For the probe molecule, we use the same interaction potentials⁴² as those in previous works.^{17,40} Because of the large mass that we use for the atoms of the model molecules, our density is relatively large. The density is set constant at $\rho = 2.24 \text{ g/cm}^3$. With these parameters, below $T = 38 \text{ K}$, the system falls out of equilibrium in our simulations; that is, $T = 38 \text{ K}$ is the smallest temperature for which we can equilibrate the system when the chromophore does not isomerize. As a result, above that temperature the medium behaves as a viscous supercooled liquid in our simulations and below that temperature it behaves as a solid (as $t_{\text{simulation}} < \tau_a$). We evaluate the glass-transition temperature, T_g , to be slightly smaller $T_g \approx 28 \text{ K}$ from the change of the slope of the potential energy evolution with the temperature. We use the Gear algorithm with the quaternion method³² to solve the equations of motions with a time step $\Delta t = 10^{-15} \text{ s}$. The temperature is controlled using a Berendsen thermostat.⁴³ We model the isomerization as a uniform closing and opening of the probe molecule shape^{16,17,39,40} during a characteristic time $t_0 = 1 \text{ ps}$. The period of the isomerization *cis*–*trans* and then *trans*–*cis* is also fixed in the study $\tau_p = 1 \text{ ns}$. In a previous work⁴⁰ we studied in detail the effects of the isomerization period, τ_p , on our results. We find that with this large period an isomerization does not influence the behavior of the system long enough to affect the next isomerization effect. That means that our period is large enough for each isomerization to be an independent process. Because of this result we do not find any aging in our system, and we find that the diffusion is proportional to the number of isomerization per second. During the isomerization the shape of the molecule is modified slightly at each time step using the quaternion method with constant quaternion variations, calculated to be in the final configuration after a 1 ps isomerization. This method corresponds to opposite continuous rotations of the two parts of the molecule that are separated by the nitrogen bonding. We model the isomerization to take place at periodic intervals whatever the surrounding local viscosity. This approximation has recently been validated experimentally¹⁵ as the pressure that is necessary to stop the azobenzene isomerization is very large ($P > 1 \text{ GPa}$).

Figure 1 shows the chromophore in the *cis* configuration. We call $L_{||}$ the length of the chromophore and L_{\perp} its width, as shown in the Figure, and we call ϕ the opening angle of the

chromophore. Then, from these quantities we define the angle $\theta = \pi - \phi$. We add the indice 0 for quantities corresponding to the real cis isomer (i.e., to the full isomerization). Thus, $\theta = 0$ when there is no isomerization and $\theta = \theta_0$ when the chromophore isomerizes to its real cis form. We then define the degree of isomerization as $p = \theta/\theta_0$. The chromophore size modification in the direction of its axis is $\Delta x_{\parallel} = L_{\parallel}^{\text{trans}} - L_{\parallel}$ and perpendicularly to that axis $\Delta x_{\perp} = L_{\perp} - L_{\perp}^{\text{trans}}$.

III. RESULTS AND DISCUSSION

Figure 2 shows the radial distribution functions (RDFs), $g_{\text{DR1-host}}(r)$, between the chromophore in the cis configuration

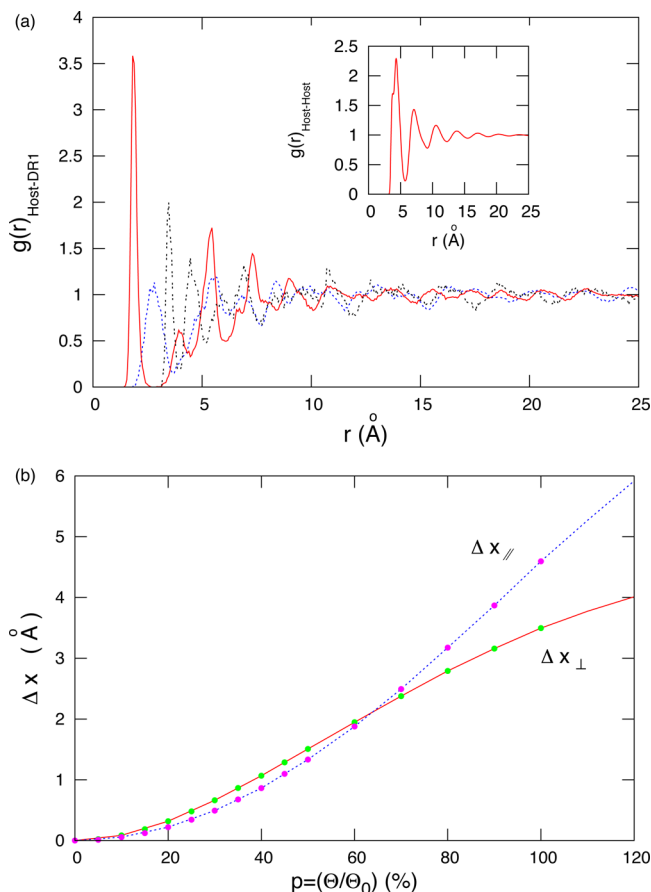


Figure 2. (a) RDF between the chromophore center of mass and the hosts molecules centers of mass for various angles θ (cis isomer), that is, various amplitudes of isomerizations $p = \theta/\theta_0$. From the left- to the right-hand sides (first peak): red continuous line, $p = 100\%$ ($\theta = \theta_0$); blue dotted line, $p = 50\%$; black dashed line, $p = 0$ ($\theta = 0$). The temperature is $T = 40$ K. Inset: Radial distribution function between the host molecules centers of mass at the same temperature. (b) Evolution of the DR1 chromophore width (Δx_{\perp}) and length (Δx_{\parallel}) with the angle θ (i.e., the isomerization amplitude p). θ_0 is the angle of the true DR1 cis isomer. Note that as the motion is not planar the angle θ is not sufficient to calculate Δx_{\perp} and Δx_{\parallel} ; however, because we use the same closing process in all the simulations, each value of θ corresponds in our work to only one value of Δx_{\perp} or Δx_{\parallel} .

and the surrounding host molecules for various isomerization amplitudes, p . We see that the first peak of the RDF is shifted from 4.0 Å for no isomerization (black line, $\theta = 0$, $p = 0$) to 1.8 Å for a full isomerization (red continuous line, $\theta = \theta_0$, $p = 1$), resulting in a 2.2 Å mean molecular displacement. The blue line in between these two peaks corresponds to a $p = \theta/\theta_0 = 50\%$

opening of the cis isomer. Note, however, that these curves represent averages taking into account the whole distribution of molecules around the DR1 chromophore, after the stabilization of the molecule positions, thus resulting in smaller variations of the distances than the ones transiently experienced by the most affected molecules. The inset shows the RDF $g_{\text{host-host}}(r)$ between the host molecules center of masses and thus represents the medium mean structure. From that curve we see that a $\Delta r = 2.7$ Å motion (the distance between the two first peaks) is enough to push completely a molecule from the first neighbor shell to the second neighbor shell. The motion of a molecule to the second neighbor shell will then destabilize that shell, inducing diffusion. The RDF between the dye and the host in Figure 2a shows that behavior, as during the isomerization the different shells of neighbors are modified in the Figure.

For smaller Δr values, even when not large enough to induce diffusion on its own, the induced motion may be able to help Brownian motion to induce diffusion. That process will depend on the temperature. To evaluate the transient motions that generate the DR1 isomerizations inside the medium, we show in Figure 2b the evolution of the chromophore width (Δx_{\perp}) and length (Δx_{\parallel}) with the characteristic angle θ (displayed as percentages of the characteristic angle, θ_0 , of the true cis isomer of the DR1 molecule). We obtain these values from the locations of the different atoms of the “partial cis” chromophore molecule. The Figure shows that the distances Δx_{\perp} and Δx_{\parallel} evolve more slowly than the characteristic angle, θ , for small values of θ . Displaying the mobilities versus θ will thus amplify artificially the thresholds. To be more accurate in the following, we will thus systematically plot our curves as a function of the change in size of the chromophore (Δx_{\perp} and Δx_{\parallel}) instead of the characteristic angle. The Figure shows that Δx_{\perp} varies between 0 and 4 Å and Δx_{\parallel} varies between 0 and 6 Å. There is thus no doubt that for large enough θ values the DR1 chromophore pushes some host molecules at distances larger than the position of the potential barrier of the cage. As a result, an isomerization-induced cage-breaking mechanism is clearly possible under the conditions of our study.

Figure 3 shows for various temperatures the evolution of the host molecule diffusion with the isomerization amplitude, p . The Figures show the existence of a threshold displacement value, $\Delta x_{\perp}^{\text{threshold}}$, a result in good agreement with the cage-breaking picture¹⁷ and the gradient pressure theory.^{26,27} For larger isomerization amplitudes (i.e., induced displacements $\Delta x_{\perp} > \Delta x_{\perp}^{\text{threshold}}$), the diffusive motions increase linearly with Δx_{\perp} , while they follow a slightly more complicate evolution with Δx_{\parallel} . This behavior is particularly visible from a comparison of Figure 3 a,b above T_g ; however, we found it less apparent at lower temperatures. Nevertheless, these differences between the evolutions suggest that the perpendicular motion of the chromophore (measured by Δx_{\perp}) mainly induces the diffusion because the linear dependence of ΔD with Δx_{\perp} suggests that Δx_{\perp} is the determinant parameter. The threshold value increases from $\Delta x_{\perp} = 0.25$ Å at $T = 40$ K to $\Delta x_{\perp} = 2.6$ Å at $T = 10$ K. This threshold dependence with the temperature suggests that Brownian thermal motions facilitate the isomerization-induced cage-escaping process. In the cage-breaking picture, at the low temperature limit, we expect the threshold to tend to a value $\Delta x_{\perp}^{\text{limit}} \approx 2.75$ Å that corresponds to the distance between the first two peaks of the RDF $g_{\text{host-host}}(r)$, as previously discussed. Consequently, the 2.6 Å value observed at the lowest temperature studied fits

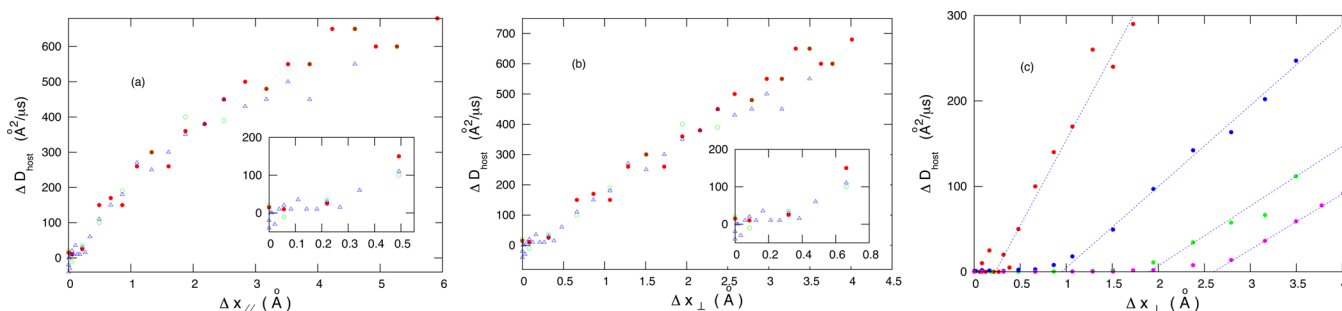


Figure 3. (a) Diffusion coefficient for host molecules, obtained from various isomerization amplitudes p and displayed as a function of Δx_{\parallel} . The different symbols correspond to different simulations: red full circles ($N = 300$, $t_{\text{run}} = 200\text{ ns}$) and blue empty triangles and green empty circles ($N = 800$, $t_{\text{run}} = 100\text{ ns}$). The calculation of D is restricted to host molecules located at a distance $R < 10\text{ \AA}$ from the chromophore. The temperature in our model is $T = 40\text{ K}$ ($T > T_g$). Inset: Details of the same curves for small Δx_{\parallel} values, showing the existence of a threshold. (b) As in panel a but the diffusion coefficient is here plotted versus the chromophore width, Δx_{\perp} . Inset: Details of the same curves for small Δx_{\perp} values. (c) Diffusion coefficient for host molecules, obtained from various isomerization amplitudes, p , and displayed as a function of Δx_{\perp} for different temperatures. From the left- to the right-hand side: red full circles, $T = 40\text{ K}$ ($N = 300$, $t_{\text{run}} = 200\text{ ns}$); blue full circles, $T = 30\text{ K}$ ($N = 300$, $t_{\text{run}} = 400\text{ ns}$); green full circles, $T = 20\text{ K}$ ($N = 300$, $t_{\text{run}} = 200\text{ ns}$); and purple full circles, $T = 10\text{ K}$ ($N = 300$, $t_{\text{run}} = 200\text{ ns}$). For these low temperatures, the threshold is more clearly visible. From this Figure, using linear fits, we find for $T = 40\text{ K}$: $\Delta x_{\perp}^{\text{threshold}} \approx 0.25\text{ \AA}$; for $T = 30\text{ K}$: $\Delta x_{\perp}^{\text{threshold}} \approx 0.95\text{ \AA}$; for $T = 20\text{ K}$, $\Delta x_{\perp}^{\text{threshold}} \approx 1.9\text{ \AA}$; and for $T = 10\text{ K}$, $\Delta x_{\perp}^{\text{threshold}} \approx 2.6\text{ \AA}$.

particularly well with the isomerization-induced cage-breaking picture. Above the threshold the diffusion increases linearly with the stimuli Δx_{\perp} with a slope that depends on temperature at high enough temperature but then tends to a constant in the low temperatures limit. Using a first-order Taylor expansion around the threshold, we find

$$D = D_0 + (\Delta x_{\perp} - \Delta x_{\perp}^{\text{threshold}})(\partial D / \partial \Delta x_{\perp})_{\text{threshold}} \quad (1)$$

where D_0 is the diffusion coefficient at the threshold, that is, the spontaneous diffusion coefficient. Then, from the relation $D = D_1 e^{-E_a/k_B T}$ ($E_a(T)$ is the activation energy) that holds for spontaneous diffusion and as $D^{\text{threshold}} = D_0$ we obtain

$$(\partial D / \partial \Delta x_{\perp})_{\text{threshold}} = (-\partial E_a / \partial \Delta x_{\perp})(D_0 / k_B T) \quad (2)$$

The term at the left-hand side of this formula is the slope at the very beginning of the lines shown in Figure 3b,c. From that formula we obtain a rough estimate of the force, f_a , that is necessary to induce diffusion (i.e., to break the cage).

$$f_a = -\partial E_a / \partial \Delta x_{\perp} \quad (3)$$

For $T = 40\text{ K}$ in our model we find $f_a/k_B \approx 44\text{ K/\AA}$. For lower temperatures the spontaneous diffusion coefficient value uncertainty is too high to use the formula. Note that in the low-temperature limit the coefficient $D_0/k_B T$ tends to zero, and as a result the slope around the threshold will tend to zero. We observe that behavior on the last curve in the right-hand side of Figure 3c, leading to some uncertainty on the position of the threshold for that curve.

Figure 4 shows the mean square displacements (MSD) of the host molecules for various isomerization amplitudes, p . The curves display a ballistic behavior on short time scales, followed by a plateau characteristic of the molecules caging and finally a diffusive time scale for some curves, while others, at the bottom of the Figure, stay in the plateau regime. These behaviors are characteristic of supercooled and glassy materials, showing that even when the isomerization is on, the host material located around the chromophore ($R < 10\text{ \AA}$) behaves as a medium below its melting temperature under the conditions of our simulations.

The first curves at the bottom of the Figure (corresponding to $p < 40\%$) are roughly flat and lead to constant values of the

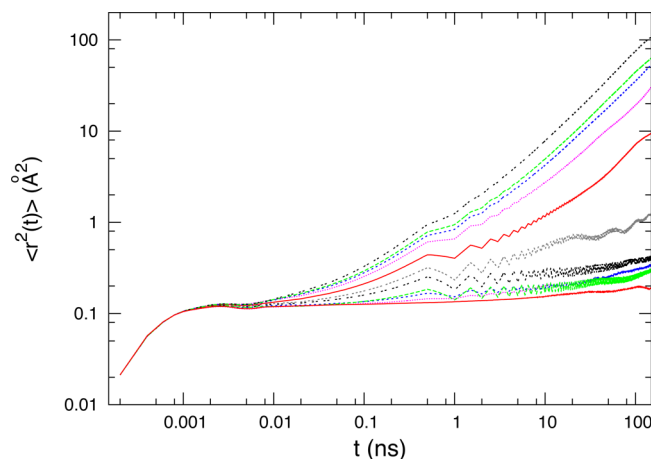


Figure 4. Mean square displacement of the host molecules for isomerization amplitudes, p . $T = 20\text{ K}$ ($T < T_g$) and there is $N = 300$ host molecules together with one DR1 molecule in the simulation box. From bottom to top: red continuous line, $p = \theta/\theta_0 = 0$; pink dotted line, $p = 10\%$; blue dashed line, $p = 20\%$; green dashed line, $p = 30\%$; black dashed line, $p = 40\%$; gray dotted line, $p = 50\%$; red continuous line, $p = 60\%$; pink dotted line, $p = 70\%$; blue dashed line, $p = 80\%$; green dashed line, $p = 90\%$; and black dashed line, $p = 100\%$. The small decrease in the green curve above 50 ns is a fluctuation. Minor ticks correspond to a factor 2, 5, and 8 to the major tic they follow.

MSD on long time scales. This behavior shows that the host molecules do not diffuse for $p < 40\%$, but we observe oscillations showing that the molecules move periodically around their equilibrium positions. Figure 4 thus shows that below a threshold $p = 40\%$, the isomerizations push the host molecules periodically inducing oscillating motions that are not large enough to induce diffusion; that is, the molecules move but stay inside their cages. These oscillations increase with the stimuli p eventually inducing diffusive motions when $\Delta r^2 > 0.4\text{ \AA}^2$. Interestingly enough, that result corresponds to the Lindemann criterion of a vibration amplitude, Δr , reaching $\sim 10\%$ of the nearest-neighbor distance, d , at the melting point as $\Delta r_{\text{threshold}} \approx 0.2\text{ \AA}$ and $d = 2.7\text{ \AA}$. Figure 4 also shows that the plateau time range of the MSD decreases when the stimuli increases (i.e., p increases or equivalently Δx_{\perp} increases).

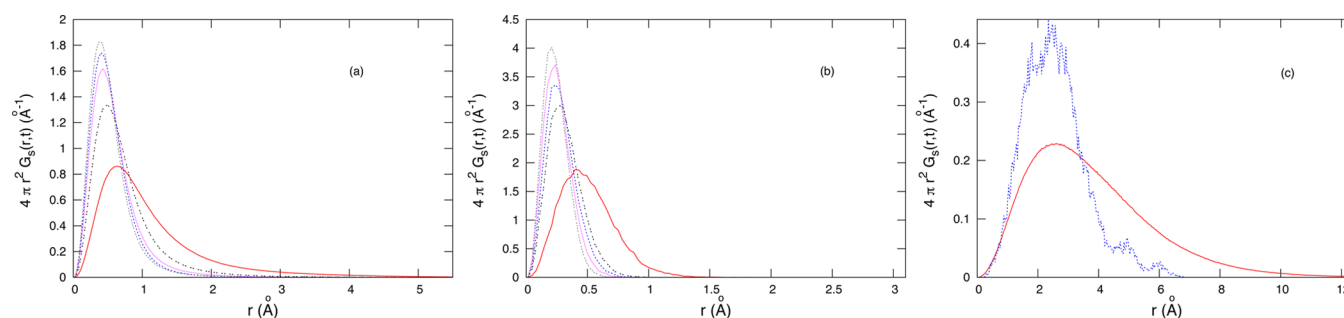


Figure 5. (a) Self van Hove correlation function $G_s(r,t)$ of the host molecules for various isomerization amplitudes, p . The van Hove represents the distribution probability to find a molecule at time, t (here $t = 2.4$ ns), a distance, r , apart from its position at time zero. $T = 40$ K, $N = 800$ host molecules and one DR1. From the left-hand side to the right: gray dashed curve, $p = 0\%$; blue dashed curve, $p = 10\%$; pink dashed curve, $p = 20\%$; black dashed curve, $p = 30\%$; and red continuous curve, $p = 40\%$. The molecules do not diffuse below $p = 30\%$. (b) As in panel a but for the chromophore molecule. From the left-hand side to the right: gray dashed curve, $p = 0\%$; pink dashed curve, $p = 10\%$; blue dashed curve, $p = 20\%$; black dashed curve, $p = 30\%$; and red continuous curve, $p = 40\%$. The chromophore does not diffuse below $p = 40\%$. (c) Self van Hove correlation function $G_s(r,t)$ ($t = 2.4$ ns) of the host molecules compared with the van Hove of the chromophore for $p = 100\%$. $T = 40$ K, $N = 800$ host molecules and one DR1. Blue dashed curve, chromophore; red continuous curve, host. The host van Hove function is characteristic of liquids continuous diffusive motions, while hopping solid-like motions are present in the chromophore's van Hove function.

However, the very beginning of the departure from the plateau, that is, the beginning of the cage-escaping process, appears around 10 ps, while the plateau begins at $t_0 = 1$ ps. The height of the plateau also increases with the stimuli. This result suggests two possible scenarios: (i) The size of the cages (that the plateau height measures) increases with the stimuli. However, the constant density of the simulations contradicts that picture. (ii) A few molecules escape the cages, increasing the mean plateau height, while most molecules still stay inside the cages. In that picture, the number of molecules escaping their cages increases with the stimuli, increasing the mean plateau height.

To gain more insight into the diffusive process, we display in Figure 5 the Self van Hove correlation functions for the host molecules (Figure 5a,c) and for the chromophore (Figure 5b,c). The van Hove correlation function measures the distribution probability for a molecule to be a distance, r , apart from its initial position after a time lapse, t . Figure 5a shows that the host molecules stay inside their cages for isomerization amplitudes below a threshold value (for $p = \theta/\theta_0 < 30\%$, the distribution probability stays centered around the same value as that when the isomerization is off, and the probability for molecular motions larger than 2.7 Å is almost zero) while they move outside the cages for larger isomerization amplitudes. The motions of the chromophore (see Figure 5b) display an even more marked isomerization amplitude threshold. The Figure shows that the chromophore only diffuses above a threshold value $p = \theta/\theta_0 = 40\%$ while the host molecules diffuse for values of p above 30% . We interpret the larger threshold for the chromophore as being due to its larger size compared with the host. Because of that larger size of the chromophore, more than one host molecule has to move to allow the diffusion of the chromophore outside its cage, leading to a larger threshold for diffusion. The large mass of the DR1 chromophore in comparison with the host molecules also explains the difference in the mobilities of the two sort of molecules when the threshold is passed. When compared with the host molecular motions in Figure 5c, for a full isomerization ($p = 1$; $\theta = \theta_0$), we see that the motion of the chromophore is much smaller than the host motion. We also observe the appearance of hopping motions for the chromophore that are not present in the host molecule motions. This behavior is

interesting enough as hopping motions are characteristic of solids while continuous diffusive motions are characteristic of liquids.

IV. CONCLUSIONS

We have studied the effect of a modification of the stimuli on the isomerization-induced transport in azobenzene-containing materials. We found that the diffusion does not increase continuously with the stimuli but that there are stimuli thresholds below which the repeated isomerizations do not induce diffusion in the material. When the temperature decreases we found that the stimuli threshold increases, suggesting that thermal-activated processes facilitate the diffusion. Above the threshold value the diffusion then increases linearly with the stimuli. The MSDs show, below the threshold, induced oscillations of motions that increase with the stimuli. At the threshold, we found oscillations amplitudes around 13% of the nearest neighbor distance ($\Delta r \approx 13\% \cdot d$), a result that recalls the Lindemann criterion for melting. These results support two models, the induced cage-breaking mechanism¹⁷ and the gradient pressure theory,^{26,27} as the origin of the isomerization-induced diffusion in azobenzene-containing materials.

AUTHOR INFORMATION

Corresponding Author

*E-mail: victor.teboul@univ-angers.fr.

Notes

The authors declare no competing financial interest.

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