Effect of double bonds on the dynamics of hydrocarbon chains

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Brownian dynamics simulations of isolated 18-carbon chains have been performed, both for saturated and unsaturated hydrocarbons. The effect of one or several (nonconjugated) double bonds on the properties of the chains is discussed in terms of both equilibrium and dynamic properties. The introduction of a *cis* double bond increases the relaxation rates of the unsaturated chain with respect to the saturated alkane. On the other hand, coupling effects in the torsional transitions around a *trans* double bond make the dynamics of this unsaturated chain very similar to the saturated one. Based on these results, the parameters and moves of a dynamic Monte Carlo algorithm are tuned to reproduce the observed behavior, providing an efficient method for the study of more complicated systems.

I. INTRODUCTION

The study of the conformational properties, dynamics, and relaxation phenomena on hydrocarbon chains and macromolecules has received a lot of attention during the last few years.[1] Both theoretical[2,3] and computer simulation investigations[4,5] have focused on the role played by the transitions between the different rotational isomeric states. As a result of these investigations, together with careful experimental measurements,[6] the global and local dynamics of linear saturated hydrocarbon chains is beginning to be understood.

On the other hand, the effect of nonconjugated double bonds on the dynamics of the chains has received considerably less attention. In some studies of long polymers, the double bond and its associated carbons are included in the model as a single unit.[7] While this simplification seems to be valid for the study of long chains, it does not result in a valid description of the dynamic behavior of relatively short, unsaturated hydrocarbon chain molecules. There is an important reason for this. In a single bond attached to other two single bonds in a linear saturated chain (sp^3–sp^3 bond), the torsional potential can be quite precisely defined by the rotational isomeric state model, with one deep minimum for the energy in the *trans* state, and two less pronounced minima for the *gauche* states. The energetic values corresponding to these minima, the barriers between them, and the higher barrier appearing for the *cis* conformation vary slightly depending on the chain length and the specific details of the model under consideration, but the essential features of the potential and the distribution of states it produces remain approximately constant. On the other hand, the picture for the rotational states of a single bond adjacent to one double bond and one single bond along an unsaturated chain (sp^2–sp^3 bond) is rather different.[8,9] Both the location of the barriers and the minima with respect to the torsional angle are substantially different from the saturated chain case. In addition, the height of the barriers is also quite reduced, which translates into larger rotational freedom around these bonds, that could compete with the rigidity imposed by the double bond itself. Therefore, the comparison of the resulting dynamics with that of the saturated chain remains uncertain. For these conditions, computer simulations may provide some insight into the process.

This question was previously addressed by us[10] in a Monte Carlo dynamics (MCD) study of molecular motions in unsaturated hydrocarbon chains. That study made use of the high coordination {210} lattice for the simultaneous representation of saturated and unsaturated chain segments. The underlying assumption of this method is that the conformational dynamics of saturated chains arise from local rearrangements involving the transfer of a single methylene group, chosen at random, to a different lattice site. However, the rigidity of the unsaturated segment necessitated the introduction of larger scale moves which involve the directly bonded methylene groups. The results are then strongly dependent on the choice of the lattice moves, particularly for the unsaturated segment, and some doubts arise about the conclusions resulting from these MCD simulations.

In order to check their validity, to correct the MCD algorithm if necessary, and especially to try to address the question of the difference in properties between saturated and unsaturated chains, we have performed a full set of Brownian dynamics (BD) simulations of isolated linear chains of 18 carbons, with none, one, two, and three double bonds, both in the *cis* and *trans* conformations, whose results are reported in this paper. The simulation scheme employed here is similar to some previously employed in the consideration of saturated chains,[4] and is simpler than other more sophisticated algorithms developed for the study of semirigid chains.[11] Thus, instead of once more

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studying the rates of torsional transitions around single bonds, we focus our attention on the influence that the double bond exerts on these transitions and its larger scale effect on certain aspects of the global dynamics of the chain, similar to the previous MCD paper.[10] Our BD results indicate quite clearly that the introduction of a *cis* double bond speeds up the chain dynamics, while the introduction of a *trans* double bond has a reduced effect on the global dynamics. In light of this conclusion, the MCD model is revisited in order to make it more in accord with the BD simulations.

II. METHODOLOGY OF THE BROWNIAN DYNAMICS SIMULATIONS

We have employed a united atom model, in which the 18 identical units of the hydrocarbon chain model are assumed to represent both methyl and methylene groups (as well as CH groups in those units which delimit the double bonds). These units are joined by 17 bonds, whose lengths are constrained to their equilibrium distances: 1.538 Å for $-CH_2-CH_2-$ bonds (sp^3-sp^3), 1.514 Å for $=CH-CH_2-$ bonds (sp^2-sp^3), and 1.316 Å for the double bond itself (sp^2-sp^2). The equations of motion (in which the free-draining limit was assumed) have been integrated by means of the Ermak–McCammon algorithm,[12] with the constraints for the bond lengths being satisfied through the SHAKE procedure[13] after every iteration.

The set of intramolecular interactions formulated for the model includes both interactions along the backbone and "long-range" interactions beteen units close in space but far apart in the chain sequence. They represent contributions to the total potential of the system based on the bond angle energy, the torsional angle energy, and the nonbonded pairwise interactions between units separated by four or more bonds.

(1) *Bond-angle potential.* The bond-angle potential is defined through the common harmonic expression

$$U_\theta = \tfrac{1}{2}k_\theta (\cos\theta - \cos\theta_0)^2, \qquad (1)$$

where $k_\theta = 520$ kJ mol^{-1} and $\theta_0 = 114.6°$ (Ref. 14) for the sp^3 carbons, while k_θ is doubled and $\theta_0 = 120°$ for the sp^2 carbons.

(2) *Torsional potential.* In this case, as stated in the Introduction, we have to distinguish several situations, corresponding to the different carbons that bracket the bond whose rotation is being considered.

(i) Bond between two sp^3 carbons. We use the expression for the rotational isomeric state potential given by Toxvaerd,[15] expressed in kelvin:

$$U_I(\phi)/k_B = 972.9 + 1867.5x - 536.8x^2 - 1856.3x^3$$
$$+ 1073.5x^4 - 1520.8x^5 \qquad (2)$$

with $x = \cos\phi$, and the torsional angle ϕ defined from the *trans* state $(\phi_t = 0, \phi_{g\pm} = \pm 120°)$. k_B is the Boltzmann's constant.

(ii) Bond between an sp^3 carbon and an sp^2 carbon. We use the expression proposed by Wiberg *et al.*,[9] based on *ab initio* quantum calculations for 1-butene:
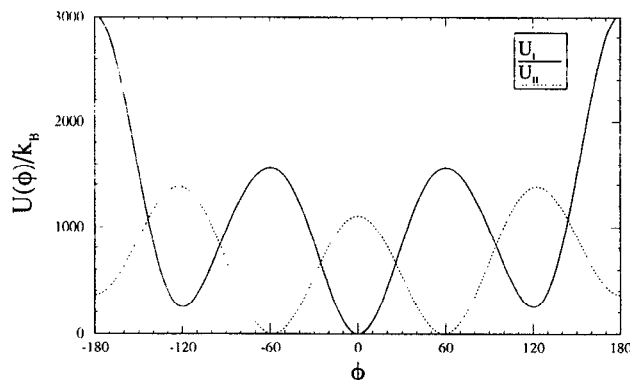

FIG. 1. Torsional potential for a single bond surrounded by single bonds (U_I) and adjacent to one double bond (U_{II}).

$$U_{II}(\phi)/k_B = \tfrac{1}{2}\{-427.8(1+\cos\phi) - 55.36[1-\cos(2\phi)]$$
$$+1162.6[1+\cos(3\phi)]\}, \qquad (3)$$

where the torsional angle ϕ is defined as in Eq. (2).

(iii) Bond between two sp^2 carbons. The rotation around a double bond is avoided by the electronic structure of the bond. In order to try to reproduce this effect, we have used an artificial form for the potential

$$U_{III}(\phi) = \tfrac{1}{2}k_\phi (\cos\phi - \cos\phi_0)^2, \qquad (4)$$

where we have made $k_\phi = 10k_\theta$, a value that gives a narrow range of torsional angles about the desired ϕ_0 (which is equal to zero when the double bond is in the *trans* conformation and equal to $\pm 180°$ when it is in the *cis* conformation). In order to appreciate the difference between the torsional potentials given by Eqs. (2) and (3), they are plotted together in Fig. 1 (in Fig. 1, U_{II} has been shifted by a constant in order to have its deepest minimum at the value $U=0$). In the following sections, we shall discuss the effects of this difference on the conformational and dynamic properties of the chains under consideration.

(3) *Nonbonded pairwise potential.* For all the residues separated by four or more bonds, we use the usual Lennard-Jones potential given by Ryckaert and Bellemans,[16] with parameters $\epsilon/k_B = 72$ K and $\sigma = 3.923$ Å. To increase the speed of the algorithm, this potential has a cutoff distance of 2.5σ.

The temperature used in the simulations is $T = 497.5$ K. This temperature is considerably high, even higher than the boiling point of some of the octadecenes modeled by our chains; however, we think it does not distort the conclusions provided by our results. In addition, because it allows for faster transitions between the different torsional states, the resulting dynamics is more tractable from the computational point of view. On the other hand, the time step is not as well determined. According to the BD algorithm employed, the ratio between the real and reduced time steps is given by the equation $\Delta t = \Delta t^* \xi(b^0)^2/(k_B T)$ and thus depends on ξ, the frictional radius of the model units, and on b^0, the average distance for every bond. Assuming identical spherical units that
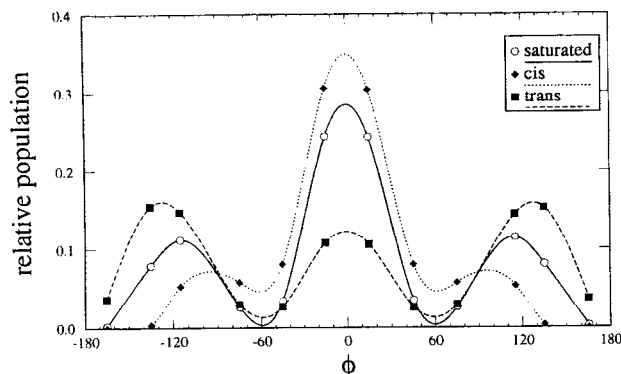
FIG. 2. BD effective populations of the torsional states for the single bonds adjacent to the 9–10 bond. The discrete points correspond to a histogram analysis based in 30° bins. The continuous lines result from a spline interpolation.

follow the Stokes behavior, $\xi = 6\pi\eta_0 r$ (with η_0 the solvent viscosity and r the radius of every unit), the value of η_0 corresponding to water, and $r \sim b^0/2 = 0.77$ Å, we get that the reduced time step $\Delta t^* = 0.0002$ we have employed is approximately equivalent to $\Delta t \simeq 1$ fs, and the reduced unit of time, $t^* = 1$, is of the order of 5 ps. The total length of the trajectory is comprised of 20 million steps, which are recorded every 2000 steps, after five million initial steps used to relax the chain from its original random conformation. Moreover, for every chain we have computed a minimum of five (a maximum of ten) trajectories, beginning with different initial conformations. Each trajectory requires about 40 h of CPU time in a Sun Sparc2 workstation.

III. BROWNIAN DYNAMICS EQUILIBRIUM PROPERTIES

The first interesting effect of the introduction of the double bond appears in the conformational properties of the chains. This effect is expected to be maximum in the properties of the sp^3-sp^2 bonds, as a consequence of their different torsional potentials. However, this potential exhibits some special characteristics. Namely, for the *cis* unsaturated double bonds, it is difficult for both single adjacent bonds to simultaneously occupy the minimum at the *cis* conformation. (In what follows, we shall use the term "unsaturated" together with the configuration of the double bond in order to avoid confusions with the torsional states of saturated bonds close to the double bond.) Therefore, the coupling between the torsional potential and the pairwise interactions can complicate the behavior of the system, an effect that also appears as the so-called "pentane effect" of completely saturated chains. The result of this coupling is the existence of an *effective potential* that, although not explicitly formulated into the model, can be considered to be actually responsible for the observed properties. In order to get an idea about the main characteristics of this effective potential for saturated and unsaturated chains, we compare in Fig. 2 the population of the different torsional angles corresponding to a saturated

chain and one with a double bond between units 9 and 10, both in the *cis* and *trans* unsaturated conformations. The connection between the effective potential and the depicted populations is simply the Boltzmann exponential. The populations shown correspond to the average of the single bonds 8–9 and 9–10 and, in addition, they are averaged over all the trajectories computed for a given chain. Obviously, the saturated chain follows the expected trend, being a qualitative reflection of the torsional potential (although the population of the *gauche* states is somehow reduced, due to the pentane effect). The unsaturated chains, however, require a more detailed exposition.

For the *cis* unsaturated chains (a short way of referring to a chain with one double bond in the *cis* conformation), the excluded volume interactions between units completely preclude any possibility of the *cis* conformation for the single bonds, even though it corresponds to a minimum in the torsional potential. As a matter of fact, the excluded volume interactions seem to be mostly responsible of the observed distribution, and this explains the high population for the *trans* state of the single bond, which is even larger than the corresponding saturated chain. (As shown in Fig. 1, the *trans* state adjacent to a *cis* double bond is disfavored based on the internal rotational potential alone.) Consequently, the final balance produces a range of torsional states which, although being narrower than the saturated chain population (since it goes to zero before reaching the *cis* barrier), has almost negligible effective barriers between the *gauche* and the *trans* states. This fact, as we shall show later, has an important consequence for the dynamics.

The situation for the *trans* unsaturated chains is rather different. The conformation of the double bond itself keeps the adjacent residues far apart. Still, the interaction between the chain tails is strong enough to reduce the population of the *cis* conformation in the single bonds attached to the double bond. Nevertheless, this population is not zero as happens in the cases considered so far. As a consequence, transitions of the type $g^+ \leftrightarrow g^-$ play a small but non-negligible role in the dynamics of these bonds. However, the most remarkable feature of the resulting effective distribution is the strong reduction in the *trans* population in the single bonds around the double bond. This is an important fact, with a dramatic effect in the equilibrium properties of the chain. One could intuitively expect that the presence of a *cis* double bond would "shrink" the global dimensions of the chain with respect to the saturated chain, while a *trans* double bond would increase the average dimensions. However, since the introduction of a *trans* double bond is accompanied by two single bonds with a strong preference towards non extended conformations, this result could be reversed. This is exactly what our simulations show, as can be observed from the values of the end to end distance $\langle R^2 \rangle^{1/2}$ and the root-mean-square radius of gyration $\langle S^2 \rangle^{1/2}$ presented in Table I. For both *cis* and *trans* unsaturated chains, the larger the number of double bonds, the smaller the dimensions. The tendency is clearly more evident in the *cis* unsaturated chains, indicating that the increased *trans* population for the single bonds

TABLE I. Average dimensions for all the studied hydrocarbon chains.

Chain	$\langle R^2 \rangle^{1/2}$ (Å)	$\langle S^2 \rangle^{1/2}$ (Å)
Saturated	13.52±0.07	4.92±0.01
cis 9=10	13.18±0.04	4.80±0.01
cis 9=10/12=13	11.66±0.05	4.47±0.01
cis 9=10/12=13/15=16	10.60±0.05	4.32±0.01
trans 9=10	13.34±0.09	4.86±0.02
trans 9=10/12=13	12.80±0.09	4.74±0.02
trans 9=10/12=13/15=16	12.40±0.07	4.67±0.02

adjacent to the double bond does not compensate for the change in the direction of the chain backbone imposed by the double bond, especially for polyunsaturated chains. On the other hand, the increased *gauche* population for the same bonds in the *trans* unsaturated chain compensates and even slightly surpasses the stretching effect of the double bond itself, bringing, as a consequence, less extended chains.

Although the distributions are different, the observed effective barriers (or populations) appearing in these *trans* unsaturated chains between the *gauche* and *trans* torsional states of the single bonds are quite comparable to those in the saturated chain. Therefore, we can expect similar dynamics or at least a rather less pronounced effect of the double bond in the *trans* as compared to the *cis* unsaturated chains.

IV. BROWNIAN DYNAMICS RELAXATION PROPERTIES

The analysis of the global dynamics of the chains is studied following a very similar procedure to that employed in the MCD calculations.[10] Therefore, we divide the chain in segments connecting non-neighbor units and study the relaxation of the vectors spanned by them. Specifically, the relaxation of the vectors joining the instantaneous positions of units 1–5, 5–9, 10–14, 14–18, and 7–12 is examined. For both saturated and 9–10 monounsaturated

chains, the behavior of bonds 1–5 and 5–9 should be symmetrical to that of bonds 14–18 and 10–14, respectively. Our simulations reproduce this expectation, demonstrating that the sampling is adequate. We have then calculated the time-correlation function

$$G_1(t) = \frac{\langle \cos \beta(0) \cos \beta(t) \rangle}{\langle \cos^2 \beta(t) \rangle} \tag{5}$$

for each of the aforementioned chain segments. The angle β defines the orientation between the segment vectors and a fixed reference direction in space. In order to further check the correctness of the trajectories, we used the three Cartesian directions as a reference, computing the corresponding correlation functions independently. Within the statistical uncertainties resulting from this analysis, we did not observe any significant difference between the three orientations. The results we present here, therefore, correspond to the average over the three orientations (and, once more, over the five to ten trajectories calculated for every chain from different initial configurations). The correlation functions decay to zero in the limit of long times (although the influence of the statistical noise begins to be important at earlier times). The value of $\langle \cos^2 \beta(t) \rangle$ used as the normalization factor equals $\frac{1}{3}$, the expected result corresponding to a unit vector without orientational preferences. We should also mention that the correlation function $G_1(t)$ includes information about both the internal dynamics of the chain and the overall molecular rotation. Since this last contribution is expected to be similar for the saturated and unsaturated chains, we shall focus our discussion only in the effect of the unsaturated segments on the internal conformational transitions.

In Fig. 3 we present the comparison between the saturated and the 9=10 monounsaturated chains. First of all, it is obvious that the decay of the vectors in the tails is faster than for the inner vectors, especially for vector 7–12, whose correlation function partially reproduces the global behavior of the full chain. This is a clear reflection of the
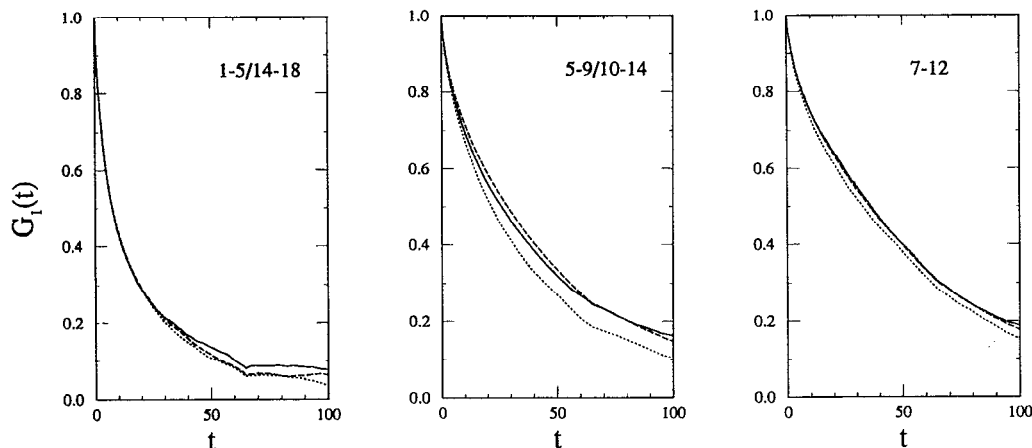

FIG. 3. Time-correlation functions for the indicated segments, computed from the BD trajectories for the saturated (solid line), *cis* 9=10 (dotted line), and *trans* 9=10 (dashed line) chains. Time scale in reduced units.

larger motional freedom existing at the ends of the chain, both as a consequence of the topology and the less pronounced effect of excluded volume restrictions for the end units. Nevertheless, the relevant discussion is the comparison between the decays of the correlation functions $G_1(t)$ for a given segment in the different chains. On one hand, for the 7–12 vector we can observe an almost identical behavior in the decay of the *trans* unsaturated chain with respect to the saturated, but there is some speed up in the *cis* unsaturated chain. For the segments 5–9 and 10–14 [whose average $G_1(t)$ is plotted in Fig. 3], the faster decay of the *cis* unsaturated chain is even more evident. On the other hand, the decays of the saturated and *trans* unsaturated chains are again very close to each other, or even a bit slower in the *trans* unsaturated case. Finally, for the tail vectors 1–5 and 14–18, the influence of the double bond is only marginal, giving at most a slightly slower decay for the saturated chain, while there is no difference between the unsaturated ones.

In order to explain these results, we can go back to the effective barriers between the torsional states whose populations are shown in Fig. 2. We have already mentioned that the effective barriers between *gauche* and *trans* states for the *cis* unsaturated chain are the lowest of the three cases considered, while there are no large differences between the *trans* unsaturated and saturated chains. This exactly translates into the dynamic behavior. For the end vectors $R1$–5 and $R14$–18, relatively far from the position where the double bond is located, there is almost no distinction between saturated and unsaturated chains, with the small differences probably being assignable to complicated couplings that relate the torsional states of neighbor bonds down the chain. On the other hand, the main effect appears for the 5–9 and 10–14 vectors, that is, those which span the chain fragment in which the sp^3-sp^2 saturated bond is included. Therefore, it is not surprising to find a faster dynamics in this fragment for chains with a *cis* double bond, while for the *trans* unsaturated chains this speed up is nonexistent. When studying the relaxation time of the 7–12 vector, we are considering the simultaneous effect of the rigid double bond and the single bonds attached to it. From the last plot of Fig. 3, it is clear that the rate enhancement of the single bonds is dominant in the *cis* unsaturated chains, although the final balance is less pronounced due to the effect of the double bond 9=10 itself. For the *trans* unsaturated chains, on the other hand, the correlation function is very similar to that observed in the saturated chain. This apparent relative insensitivity to the introduction of a *trans* unsaturated bond poses some problems since, in these conditions, the slowing effect of the double bond should prevail.

To explain the observed behavior, one has to carefully evaluate the short-range dynamics of the chains near the double bond in the different cases considered. There are a number of effects that require discussion. The first is the possible coupling between the librational motions of the torsional angles inside one single minimum of the potential, i.e., without torsional transitions, and the conformational transitions themselves. This effect has been claimed

to be important[3] in the relaxation processes of chain molecules. Probably more interesting is the difference between the transition rates between torsional states of a single bond depending on the torsional state of the adjacent bonds. Helfand *et al.*[4] proved both by simulation and theoretical studies[17] that the transition rates increase in the vicinity of a *trans* state and, even more, that an important coupling exists between the torsional transitions of two single bonds separated by a single bond in the *trans* state. Thus, the parallel orientation of these two bonds, existing in the *trans* but not in the *cis* conformation of the central bond, seems to play a very important role in the dynamics of the fragment, so much so that even fast local transitions for the first neighbors around a *trans* double bond are coupled, i.e., a simultaneous counter rotation of the single bonds at both sides of a *trans* state localizes almost completely the movement in such a way that the resulting long-range dynamics is almost unaffected.

This result (for saturated chains) has been also checked recently through molecular dynamics simulations.[5] In addition, it has been also observed that this coupling between second neighbors does not appear when they are not in a parallel conformation, that is, when the central bond is not in a *trans* conformation. This is one of the main conclusions of the simulation studies of Adolf and Ediger[18] on polyethylene and polyisoprene. In the former, a saturated chain, the population of *trans* states is dominant and, as a consequence, the second-neighbor coupling is observed. On the other hand, first-neighbor couplings play a much more important role in polyisoprene, a molecule that includes *cis* double bonds in its backbone.

Our simulations are consistent with these previous observations. As a matter of fact, additional analysis performed on the correlation functions of the different torsional angles for the single bonds corroborate rather well most of these facts. Thus, we can explain the differences existing between *cis* and *trans* unsaturated chains and the similarity between the latter and the saturated chains.

In order to quantify the effect of the double bonds into the dynamics, we have computed the correlation times τ defined as

$$\tau = \int_0^\infty G_1(t)\,dt. \tag{6}$$

Prior evaluating the integral, we fitted the functions $G_1(t)$ to a multiexponential expression, using the program DISCRETE.[19] This program uses an algorithm which does not *a priori* assume a fixed number of exponential contributions. We get in most of the cases a solution with three components (occasionally two, and very seldom four), consistent with the expression previously used in the MCD paper.[10] From this solution, the integral in Eq. (6) is trivial to calculate. The resulting relaxation times are included in Table II. The uncertainties reported are derived from the standard deviations of the parameters in the multiexponential fitting.

The comparison between the saturated and both mononounsaturated chains exactly reflects the trends we have already discussed from Fig. 3, i.e., the symmetrical behav-

TABLE II. Correlation times for the indicated intermediate vectors of the chains computed through BD simulations. The values are given in the reduced units described in the text.

Chain	$R1$–5	$R5$–9	$R10$–14	$R14$–18	$R7$–12
Saturated	21 ± 1	44.9 ± 0.2	44.2 ± 0.4	19.6 ± 0.4	55.2 ± 0.2
cis 9=10	18.7 ± 0.4	38 ± 2	38 ± 2	18.5 ± 0.2	51.6 ± 0.2
cis 9=10/12=13	18.2 ± 0.2	36.9 ± 0.2	27.0 ± 0.3	16.5 ± 0.2	39.7 ± 0.1
cis 9=10/12=13/15=16	19.4 ± 0.2	34.9 ± 0.2	27.2 ± 0.2	15.0 ± 0.1	38.9 ± 0.2
trans 9=10	19.5 ± 0.4	46.9 ± 0.2	46.3 ± 0.1	19.4 ± 0.3	55.6 ± 0.1
trans 9=10/12=13	19.0 ± 0.1	43.1 ± 0.6	40.5 ± 0.1	16.7 ± 0.3	52.9 ± 0.2
trans 9=10/12=13/15=16	18.9 ± 0.3	42.5 ± 0.3	33.7 ± 0.1	13.3 ± 0.5	48.5 ± 0.2

ior of the chains, the speeding up effect of the double bond in the *cis* unsaturated chains, and the cancellation of different opposite effects that yields an almost null global effect of the *trans* double bond. Therefore, it is more important to focus the discussion of Table II on the polyunsaturated chains, with two and three nonconjugated double bonds. First of all, it is interesting to observe that the effect of the double bond and the possible couplings it induces vanish almost completely for intermediate distances down the chain backbone. This is evident from the values of τ corresponding to the $R1$–5 fragment, which remain almost constant for all the chains. Moreover, the *cis* polyunsaturated chains seem to present results that can be rationalized from a generalization of the monounsaturated chain. Thus, the introduction of a second *cis* double bond in the 12=13 position reduces the relaxation time of $R10$–14, the segment that brackets this double bond. This effect is increased for $R7$–12, the segment which includes one of the single bonds attached to the new double bond. A small reduction in the correlation time for $R5$–9 can indicate a minor coupling in the motion of the two *cis* double bonds that extends to their close surroundings. On adding the third *cis* double bond in position 15=16, these effects again appear, but now their magnitude is greatly reduced. The interpretation might be that the effects on the chain dynamics are reaching a plateau. Therefore, the extension of these results to chains of different length or *cis* polyunsaturated macromolecules should be done carefully from the quantitative point of view, although the qualitative picture seems to be rather clear for the *cis* polyunsaturated hydrocarbon chains.

In the *trans* polyunsaturated chains, on the other hand, the effects are more subtle. While the introduction of a single *trans* double bond does not exert any important effect on the global dynamics studied in this article, the addition of more *trans* double bonds slightly speeds up the movements of the polyunsaturated chain. From the results in Table II, it can be concluded that the combined effect of the complex couplings mentioned earlier between single bonds adjacent to *trans* double bonds is now able to compensate and even overcome the rigidity of the double bond itself, so that the final effect is similar, but less pronounced, to that observed in the *cis* (poly)unsaturated chains. Even more, the apparent plateau in the effects of the cumulative double bonds is reached earlier for the *cis* than for the *trans* polyunsaturated chains. At the present moment, it is not possible to estimate whether both type of chains would

finally reach some kind of equivalent quantitative relaxation behavior with the introduction of additional double bonds in longer chains or they will just cross and exhibit independent behaviors.

Even though the correlation functions $G_1(t)$ only represent the behavior of a set of internal orientations in the chain, the dynamic picture they provide is quite accurate. As a matter of fact, the correlation function $G_R(t)$ for the end-to-end vector of the chains, which includes both the orientation and the modulus of this vector and could thus be thought as a better representation of the flexibility of the chain, gives results completely equivalent to those already discussed, without providing any new information. Therefore, we can conclude from this set of Brownian dynamics simulations that the effect of a double bond in a hydrocarbon chain is to speed up the global dynamics of the chains, an effect which is clearly observable in *cis* unsaturated chains and which is less pronounced in *trans* unsaturated chains. Since this conclusion is opposite to that previously extracted from MCD simulations,[10] and assuming the physical correctness of the BD scheme, we present in the following sections some refinements of the MC procedure designed to reproduce, at least qualitatively, the results presented so far.

V. MONTE CARLO DYNAMICS SIMULATIONS

The representation of hydrocarbon chains on the lattice has been discussed in detail previously[10] and will only be summarized here. The model hydrocarbon chain consists of N beads connected by $N-1$ bonds and is confined to a cubic lattice. On this lattice, the individual beads are separated by a distance of $\sqrt{5}$ and the bonds are obtained by a cyclic permutation of the 24 vectors of the type $\{\pm 2, \pm 1, 0\}$. One lattice unit is thus equivalent to a distance of 0.69 Å. The vectors are chosen from this basis set under the condition that the distance $R13$ between beads i and $i+2$ lies in the interval $\sqrt{10} \leqslant R13 \leqslant \sqrt{18}$. With this representation, we have admitted the existence of multiple dihedral conformational states about each bond.

The occurrence of multiple choices for the dihedral angles about the interior bonds of the model chain leads to more disordered (coiled) conformations which results in a shorter end-to-end distance than is expected for real alkane chains. We have counteracted this artificial shortening of the model chain by penalizing the probability of occurrence of effective *gauche* conformers. To this end, we im-

pose restrictions on the distance $R14$ between the ith and $(i+3)$th beads in the chain. In our algorithms we rejected configurations for which $R14 \leqslant \sqrt{5}$ and accepted configurations with $\sqrt{5} < R14 \leqslant \sqrt{30}$ with a probability of 0.3. All configurations with $R14 > \sqrt{30}$ were accepted without penalties.

This penalty scheme is designed to suppress the occurrence of distances $R13$ equal to $\sqrt{10}$ and $\sqrt{12}$. Chain configurations with these distances cannot be eliminated altogether as they form essential pathways in the conformational changes of the model chain. It is important to stress that the probability of acceptance of these states is arbitrary and is made with a view towards reproducing the end-to-end distances of real polymethylene chains. However, the severity of the penalty also affects the dynamics of the chain as reflected in the decay of the time correlation functions. In general, the correlation times increase substantially on decreasing the probability with which the distances $R14$ in the range $\sqrt{5} < R14 \leqslant \sqrt{30}$ are accepted. Nevertheless, it transpires that the relative rates of the internal modes of motion are not affected by the value used. Our choice of 0.3 is a compromise between the equilibrium and dynamic properties. We note that the probability of 0.2 used in our earlier study[10] gave rise to longer chains but slower conformational dynamics.

Excluded volume effects were implemented by surrounding each bead by 12 occupied lattice sites, forming an fcc envelope about its position. These sites were obtained from the cyclic permutation of the vectors $\{\pm 1, \pm 1, 0\}$. No other interactions between the beads entered the simulations.

The representation of the *cis* and *trans* double bond segments on the lattice was chosen so as to reproduce their rigid planar configuration. There were 48 distinct triplet vector combinations taken from the set $\{\pm 2, \pm 1, 0\}$ which satisfy this condition for the *cis* segment and 96 for the *trans*.

The basic premise of our Monte Carlo approach to the description of internal chain dynamics is that any mode of conformational motion can be mimicked by a superposition of random local rearrangements arising from the transfer of a single bead to a different lattice site. However, this assumption may not hold if collective conformational modes play an important role in determining the chain dynamics. The displacement of bead i to a new position is carried out by changing the two vectors representing the bonds $i-1$ and i in the chain. In our notation, bond i joins beads i and $i+1$. This modification of the vectors preserves the length of the bonds but effects simultaneous rotations about the bonds $i-2$ and $i+1$. The first and last bonds are allowed to undertake random orientations. These latter moves introduce new local orientations which diffuse into the interior parts of the chain. The set of local modifications described is found to span all possible conformations of the model polymethylene chain and allows the study of its dynamic properties.

The lack of rotational motions about the central double bond of the unsaturated segment $-C1-C2=C3-C4-$ necessitates the modification of the moves used for simu-

lating the dynamics of saturated chains. Now two beads C1 and C2 must be displaced simultaneously in any local rearrangement. The simplest scheme for effecting such a move is the interchange of the vectors representing the single bonds C1–C2 and C3–C4 of the unsaturated segment. However, it is important to note that this move is only effective for *cis* unsaturated segments. The orientation of a *trans* unsaturated segment is conserved under the interchange since the two bonds are parallel. Larger scale moves involving a collective displacement of a group of three beads, either C1–C2=C3 or C2=C3–C4, must be introduced in order to facilitate the displacement of bead C1 or C4 on the lattice. The reason for this is that the single bonds C1–C2 and C3–C4 form part of the rigid unsaturated segment. These moves were implemented in our previous MCD study[10] and led to the artificially slow dynamics associated with the introduction of a *cis* unsaturated double bond. As these findings are at odds with the results of BD simulations, the question now arises whether this is an artifact arising from the set of moves chosen or is an intrinsic weakness of the MCD approach.

In order to investigate this question we have enlarged the set of moves allowed for the unsaturated segment with all the possible collective displacements of beads C1 to C4 inclusive. The new moves were implemented in the following way. Each time one of the beads C1, C2, C3, or C4 is picked, new vectors are assigned to all five bonds and all four beads are moved to different lattice positions. This applies equally to the *trans* and *cis* unsaturated segments and the moves include the interchange of the single bonds C1–C2 and C3–C4 in both cases. No penalties are imposed on the distances $R14$ which span the double bond. In addition, the penalty scheme for the distances $R14$ spanning either the bond C1–C2 or C3–C4 for the *cis* unsaturated segments is relaxed slightly in order to avoid kinetic trapping effects. We note that kinetic trapping arises from the exclusion of some pathways for conformational changes. The modification of the scheme simply implies a reduction of the upper bound of the range of penalized distances $R14$ from $\sqrt{30}$ to $\sqrt{26}$.

The collective moves described earlier can only be implemented for a monounsaturated chain or a chain where the unsaturated segments are separated by at least three single bonds. The reason lies in the fact that the model moves involved the displacement of beads on the lattice. For a polyunsaturated chain of the form $-C1-C2=C3-C4-C5=C6-C7-$, a move of bead C4 implies a simultaneous displacement of both unsaturated segments, involving at least beads C2 to C6 inclusive. Consequently, large amplitude concerted motions are introduced into the chain, which in turn distort the chain dynamics. Especially for short chains, the assumption of local conformational rearrangements on which the present MCD model is based is now no longer tenable. Similar problems arise from the combination of large amplitude cooperative motions of two unsaturated segments separated by three single bonds. For this reason we believe that the MCD algorithm presented above is not suitable for simulating the conformational dynamics of polyunsaturated chains.
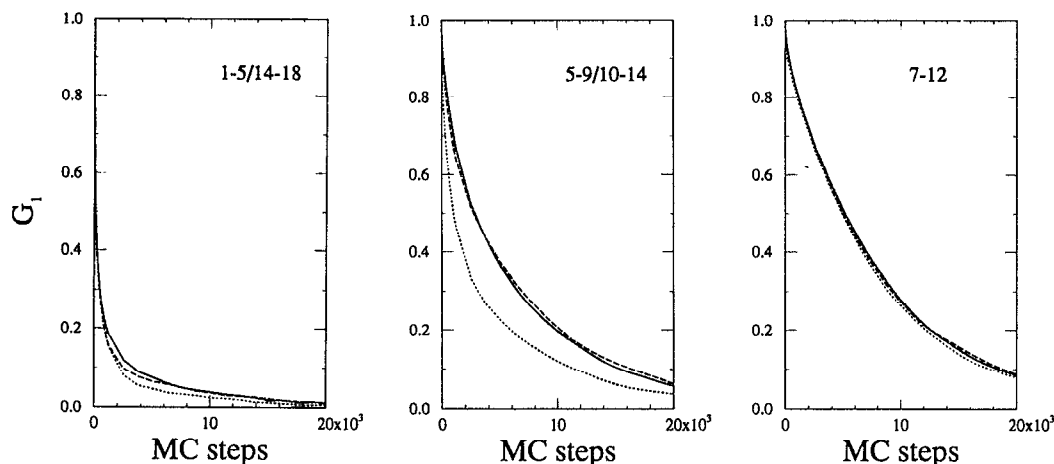
FIG. 4. Time-correlation functions for the indicated segments, computed from the MCD trajectories for the saturated (solid line), *cis* 9=10 (dotted line), and *trans* 9=10 (dashed line) chains.

Any MCD move is subjected to two acceptance tests. In the first place, the new $R14$ distances between the beads involved in the move and their neighbors are checked, and the move allowed only if it satisfies the criteria set out previously. Second, the move is only accepted if the final lattice positions of the beads are unoccupied. This test is applied to both a bead and its associated excluded volume envelope.

The Monte Carlo dynamics is implemented in the following way. Given a particular configuration of the chain, $\Phi(j)$, we attempt N local conformational moves with each bead having an equal chance of being picked. These N moves generate a new configuration of the chain, $\Phi(j+1)$. The cycle is now repeated using $\Phi(j+1)$ as the starting configuration. The fundamental time step of the algorithm is defined as the time required for the chain to undergo a transition from configuration $\Phi(j)$ to $\Phi(j+1)$. However, this approach does not relate the time step to an absolute scale.

The correlation function for motion of any chain vector, Eq. (5), is obtained from the sequence of generated configurations $\Phi(j)$'s along the time trajectory, as described earlier for the BD simulations. We have chosen the sampling interval of the trajectories to be such that the autocorrelation function decayed to its equilibrium value within 1000 sampling points. Typically, 640 000 configurations at intervals of 25 elementary time steps were used in the calculations. For every chain, we computed a minimum of five trajectories starting with different initial conformations. Each trajectory required about 90 min CPU time on a DEC3100 workstation.

VI. MCD RESULTS

MCD simulations for saturated, 9=10 *cis* unsaturated and 9=10 *trans* unsaturated chains were carried out following the scheme set out previously. The end-to end distance of the saturated chain, 13.8 Å, was found to be similar to that of 14.1 Å found for the *trans* unsaturated chain.

Nevertheless, a significantly smaller end-to-end distance of 12.9 Å was found for the *cis* unsaturated chain. While the absolute values of the end-to-end distances are clearly dependent on the penalty imposed on the $R14$ distances in the chains, the relative order of *cis* and saturated chains is in good agreement with that found from BD simulations, Table I, but the *trans* unsaturated chains are slightly too expanded.

The correlation functions evaluated from the MCD algorithm using Eq. (5) for the vectors $R1$-5, $R5$-9, $R10$-14, $R14$-18, and $R7$-12 are shown in Fig. 4. The decay of the correlation functions was found to be independent of the choice of the reference axis in space, indicating that the orientational motions of the chain segments are isotropic. The isotropy was also reflected by the uniform distribution of each bond vector over the 24 basis vectors of the lattice. The decay of the correlation functions for the $R10$-14 and $R14$-18 vectors are indistinguishable from those for the $R5$-9 and $R1$-5 vectors, respectively, thus reflecting the symmetry of the chains about their centers of mass. The corresponding correlation times obtained from Eq. (6) are given in Table III. These were obtained as described earlier from a numerical multiexponential fit of the correlation function. The best fits were obtained using a three-component decay.

The decays of the correlation functions for the saturated chain shown in Fig. 4 are similar to those presented by us previously.[10] The differences are due simply to the fact that we have here imposed a less severe penalty on the

TABLE III. Correlation times for the intermediate vectors of the chains computed by MCD. The values are given as the number of MCD steps.

Chain	$R1$–5	$R5$–9	$R10$–14	$R14$–18	$R7$–12
Saturated	1440±10	5750±20	5740±20	1430±10	7650±20
cis 9=10	1030±10	3870±15	3850±15	1035±10	7600±20
trans 9=10	1290±10	5860±20	5870±20	1300±10	7680±20

distances $R14$; the probability of acceptance is 0.3 instead of 0.2 as in Ref. 10. Interestingly, the introduction of the new collective moves for the *cis* unsaturated segment now cause the correlation function for the central vector $R7-12$, Fig. 4, to decay much faster than in our previous study.[10] Indeed, the decay of the correlation function is now even somewhat faster than that for the corresponding vector in a saturated chain. Moreover, the correlation function for the other vectors do not exhibit the long time tails reported in Ref. 10. It may be argued that the increased internal conformational motion exhibited by the *cis* unsaturated chain arises from the introduction of the collective moves rather than from the geometrical restrictions imposed by the *cis* unsaturated segment. However, the conformational dynamics of saturated chains are not affected on introducing these collective moves into the algorithm. Furthermore, we find distinctly different dynamics for the *trans* unsaturated chains, Fig. 4. These observations indicate that the differences observed between the dynamic behavior of the chains are indeed due to the effects of the unsaturated segments.

The difference between the results presented here and those reported by us in Ref. 10 is wholly due to the modifications in the rules for the allowed moves described above. The most important ingredient turns out to be the introduction of the cooperative moves for the unsaturated segment and the beads directly attached to it. This strongly suggests that concerted motions play a more important role in determining the internal dynamics of unsaturated hydrocarbon chains than saturated ones.

A comparison of Figs. 3 and 4 shows that, in general, the decays obtained from the MCD simulations track those evaluated from the BD simulations for the saturated, *cis* and *trans* unsaturated chains in the 9–10 positions. The major differences between the two approaches are to be found in the decays of the correlation functions for the vectors $R1-5$ and $R14-18$ for all three chains, and the $R5-9$ and $R10-14$ vectors of the *cis* unsaturated chain. The discrepancies probably arise from athermal nature of the MCD calculation as well as from the neglect of interactions between the beads. Nevertheless, it cannot be ruled out that the MCD scheme does not take proper account of collective modes in the chains.

The MCD results show that the introduction of a *cis* unsaturated segment into the chain causes a far larger effect than the incorporation of a *trans* segment at the same position. In particular, we find that while the *cis* unsaturated segment causes an increase in the orientational relaxation dynamics of the $R5-9$, $R10-14$, and $R7-12$ vectors, a small but significant slow down is found for chains containing a *trans* segment. The reason for this must be sought in the way the motion of the unsaturated segments introduce new local conformational rearrangements into the short saturated chain segments attached to them. The moves of the *cis* unsaturated segments introduce different local conformations on either side of the double bond. This arises simply from the fact that the two single bonds of the *cis* segments are not parallel. Any moves of the *cis* segment, whether local due to the interchange of the bond vectors,

or cooperative ones involving several atoms, effectively scramble the lattice vectors representing the two bonds. Consequently, different conformational rearrangements are introduced into the two short saturated chain segments attached to the *cis* unsaturated segment. This effectively leads to a decoupling of the conformational motions of the two segments and is manifested as a faster orientational motion of the $R5-9$ and the $R10-14$ vectors in the chain. In contrast, the two single bonds of the *trans* unsaturated segment are by definition parallel, so that the motion of this unsaturated segment now introduces the same local conformational changes on either side. This preserves, or even enhances, the diffusion of conformational changes from the one free end of the chain to the other. For this reason, the motions of the saturated and *trans* unsaturated chains exhibit similar behavior in the MCD simulations. We note, however, that the motions of the terminal segments, the vectors $R1-5$ and $R14-18$, of the chain are virtually unaffected by the introduction of an unsaturated segment in the middle 9–10 position.

VII. SUMMARY AND CONCLUSIONS

In this article we have performed a systematic study of the effect of double bonds on the dynamics of hydrocarbon chains. This study includes a careful consideration of the relations existing between the different contributions to the intramolecular potential formulated initially for the model chain and their effects on some equilibrium and dynamic properties.

Initially, the model is analyzed through Brownian dynamics simulations. These show quite clearly that a *cis* double bond introduced into a hydrocarbon chain increases the global relaxation rates with respect to the corresponding saturated chain. The introduction of additional *cis* double bonds has the same effect, although it becomes less and less pronounced. From the simulations undertaken so far, a limiting behavior seems to exist for the dynamics of polyunsaturated *cis* chains, but even a qualitative estimation of this limit is not possible at this moment. On the contrary, the *trans* unsaturated chains exhibit a dynamic behavior very similar to the saturated chains. This can be explained through coupled rotational transitions, well documented in the literature, that occur around a bond in the *trans* state (a *trans* double bond in our chains) keeping the global dynamics almost unaffected. The geometrical conformation of the *trans* bond seems to be responsible for this coupling and, thus, one can expect the conclusions to be the same for a saturated bond in the *trans* state or a *trans* double bond.

Based on these results, a previous dynamic Monte Carlo model[10] has been partially reformulated. New penalty schemes for the local conformations, which weight them in a different way, and especially the introduction of new cooperative motions for the unsaturated segments, allow for very good agreement between BD and MCD results for saturated and monounsaturated chains. This is a very important achievement, that validates considerably the MCD algorithm. One has to account for the fact that the study of short isolated chains constitutes a severe test

for a dynamic MC algorithm. Our MCD algorithm has been able to pass this test after the "calibration" procedure performed here. Therefore, one can expect that it can be very useful for the study of systems more adequately described through a MC scheme, such as certain aspects of the dynamics of multichain dense systems (e.g., lipid monolayers or biological membranes) for which BD calculations would be unrealistic based on the computational times which would be required.

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